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On a Certain Class of Fraunhofer's Diffraction-Phenomena.

By

H. Nagaoka, *Rigakuhakushi.*

The intensity of light for Fraunhofer's diffraction-phenomena is proportional to I, where

$$I = C^2 + S^2 \ ,$$

C and S being put for the surface-integrals

$$C = \iint dxdy \cos \frac{2\pi}{\lambda} \Big(x(\alpha - \alpha_0) + y(\beta - \beta_0) \Big)$$

$$S = \iint dxdy \sin \frac{2\pi}{\lambda} \Big(x(\alpha - \alpha_0) + y(\beta - \beta_0) \Big)$$

In the above expression, λ denotes the wave-length of light; α, β cosines of the angles made by the incident ray with the axes of x and y resp., α_0, β_0 those for the diffracted ray; the coordinate axes lie in the plane of the diffracting opening, over which the integration is to extend.

Putting

$$\frac{2\pi}{\lambda}(\alpha - \alpha_0) = \mu \quad , \quad \frac{2\pi}{\lambda}(\beta - \beta_0) = \nu \ ,$$

we can write

$$I = \left[\iint e^{i(\mu x + \nu y)} dxdy \right]^2 .$$

For n openings of the same size similarly situated, the expression for I is greatly simplified by means of Bridge's theorem. Denoting

the coordinates of homologous points by $a_0 b_0$, $a_1 b_1, \ldots\ldots, a_{n-1} b_{n-1}$, the expression for the intensity becomes

$$(A) \qquad I = \left[\varphi \sum_{0}^{n-1}{}_m \, e^{i(\mu a_m + \nu b_m)} \right]^2,$$

where

$$\varphi = \iint e^{i(\mu x + \nu y)} \, dx dy \, ,$$

which, integrated over any *one* of the openings, has always the same absolute value.

Introducing polar coordinates $r_m \, \vartheta_m$, we can write

$$\mu a_m + \nu b_m = \gamma r_m \cos(\vartheta_m - \delta) \, ,$$

provided

$$\gamma = \sqrt{\mu^2 + \nu^2} \, , \; tg \, \delta = \frac{\nu}{\mu} \, .$$

The expression (A) is thus transformed into

$$(B) \qquad I = \left[\varphi \sum_{0}^{n-1}{}_m \, e^{i \gamma r_m \cos(\vartheta_m - \delta)} \right]^2$$

In (A) and (B), the expression under the sign of summation depends on the relative position of the openings only, while (φ) will be known when the form and size of the opening is given.

I shall here treat of a special case of summation, whereby

$$r_m = const., \;\; \vartheta_m = m\alpha \;\; \text{and} \;\; n\alpha = 2\pi.$$

Writing $\gamma r^m = c$, we easily find by expansion

$$1) \quad \sum_{0}^{n-1}{}_m \, e^{i c \cos(m\alpha - \delta)} = n J^0(c) - i^n . \, 2n \Big(\cos(n\delta) J^n(c) + \cos(2n\delta) J^{2n}(c) + \ldots\ldots \Big)$$

when n is even ;

$$2)\quad \sum_{0}^{n-1} e^{i c \cos(m\alpha-\delta)} = n J^{\circ}(c) + i^{n}.\, 2n\Big(\cos(n\delta) J^{n}(c) + \cos(3n\delta) J^{3n}(c) + \ldots\ldots\Big)$$

$$+ i^{n-1}.\, 2n\Big(\cos(2n\delta) J^{2n}(c) + \cos(4n\delta) J^{4n}(c) + \ldots\ldots\Big)$$

when n is odd.

Supposing n is very large compared with c, we can show that the sum of the series within the brackets is negligible.

The convergent series for $J^{n}(c)$ can be written

$$J^{n}(c) = \frac{c^{n}}{2^{n}\,\Pi(n)}\Bigg[1 - \Bigg(\frac{c^{2}}{2^{2}(n+1)} - \frac{c^{4}}{2!\,2^{4}(n+1)(n+2).}\Bigg)$$

$$- \Bigg(\frac{c^{6}}{3!\,2^{6}(n+1)(n+2)(n+3)} - \frac{c^{8}}{4!\,2^{8}(n+1)(n+2)(n+3)(n+4)}\Bigg) - \ldots\ldots\Bigg]$$

If $c < 8.\,(n+2)$, the terms in parenthesis are always positive, so that

$$J^{n}(c) < \frac{c^{n}}{2^{n}\,\Pi(n)}$$

Consequently the series

$$J^{n}(c)\cos\delta + J^{2n}(c)\cos 2n\delta + \ldots\ldots\ldots\ldots\ldots$$

$$< \frac{c^{n}}{2^{n}\,\Pi(n)} + \frac{c^{2n}}{2^{2n}\,\Pi(2n)} + \ldots\ldots\ldots\ldots\ldots,$$ which again is less than $\left(\frac{ec}{2n}\right)^{n} \dfrac{1}{\sqrt{2\pi n}\left[1 - \left(\frac{ec}{2n}\right)^{n}\right]}$, a very small quantity when n is large. Similarly, we can prove that the other series within the brackets are negligible; accordingly we arrive at the result

$$\sum_{0}^{n-1} e^{i c \cos(m\alpha-\delta)} = n J^{\circ}(c) \qquad (n\alpha = 2\pi)$$

The expression for the intensity of the diffracted ray for the

following distribution of equal, similar, and similarly situated openings can be reduced to the form

$$(C) \qquad I = n^2\Big(J^\circ(c)\Big)^2 (\varphi)^2,$$

when the above mentioned conditions are satisfied.

In the following three cases, we can bring the expression for the intensity of diffracted light into form (C).

I. Suppose the homologous points of n openings are arranged in a straight line such that their coordinates are given by

$$a_m = a\cos(m\alpha - \beta) \qquad , \qquad b_m = o.$$

with the condition $n\alpha = 2\pi$. Such distribution is well illustrated by the usual diagrams of the condensation and rarefaction wave, but it is to be remarked that in the condensed part the neighbouring openings must not overlap each other. The intensity of the diffracted light is evidently given by (A) and (C)

$$I = \left[\varphi \sum_{o}^{n-1} e^{i\mu a\cos(m\alpha-\beta)}\right]^2$$

$$= n^2\Big(J^\circ(\mu a)\Big)^2 (\varphi)^2$$

If $\beta = o$ and n be an even number, every two of the openings overlap each other with the exception of the *o-th* and the $\frac{n}{2}$ th; if n be an odd number, with the exception of the *o-th*, the expression must be slightly changed.

The diffraction-figure will consist of straight lines perpendicular to the line joining the homologous points.

II. The openings are distributed on the periphery of a circle of radius a at equal angular intervals, so that

$$a_m = a\cos(m\alpha - \beta) \qquad , \qquad b_m = a\sin(m\alpha - \beta).$$

The expression for the intensity becomes

$$I = n^2 \left(J^\circ(\gamma a) \right)^2 (\varphi)^2$$

The diffraction figure arising from the given distribution consists of concentric circles whose radii are proportional to the roots of the equation

$$J^\circ(\gamma a) = o.$$

The experimental verification of this result was communicated some time ago to the Tōkyō Physico-Mathematical Society.[1]

It is remarkable that the same phenomenon can be observed in an indefinitely thin annulus of radius a. From the expression for the intensity of the diffracted light for a circular opening,

$$I_a = \left(\frac{a J^1(\gamma a)}{\gamma} \right)^2 ,$$

we easily find, for a circular annulus of breadth ∂a and radius a,

$$I_{\partial a} = \left(a J^\circ(\gamma a) \partial a \right)^2 ,$$

which shows that the same diffraction pattern will be exhibited by the annulus with the above mentioned distribution.

III. Suppose the openings are distributed at equal angular intervals along the periphery of a Pascal's limaçon whose equation is of the following form.

$$r = a + b \cos \vartheta.$$

Applying formula (B), and writing

$$r_m = a + b \cos (m\alpha - \beta) \quad , \quad \vartheta = m\alpha - \beta,$$

we find easily that

1. *Tōkyō-Sūgaku-Butsurigaku-kwai Kiji.* **5.** p. 75. 1893.

$$\sum e^{i\gamma r_m \cos(\vartheta_m - \delta)} = e^{i\gamma \frac{b}{2} \cos\frac{\delta}{2}} \sum_{0}^{n-1} e^{i\gamma\rho\cos(m\alpha - \varepsilon)},$$

where

$$\rho = \sqrt{a^2 + ab\cos\frac{\delta}{2} + \frac{b^2}{4}},$$

$$tg\,\varepsilon = \frac{a\sin(\beta+\delta) + \frac{b}{2}\sin\left(\beta + \frac{\delta}{2}\right)}{a\cos(\beta+\delta) + \frac{b}{2}\cos\left(\beta + \frac{\delta}{2}\right)}.$$

Thus the expression for the intensity of the diffracted light becomes

$$I = n^2\left(J^c(\gamma\rho)\right)^2 (\varphi)^2$$

The position of dark lines due to such distribution of the openings will be given by the roots of $J^c(\gamma\rho)=o$. With perpendicular incidence, the polar equation to the curve of zero intensity is

$$r = \frac{k}{\sqrt{p + q\cos\frac{\psi}{2}}},$$

where $$p = a^2 + \frac{b^2}{2}, \qquad q = ab,$$

and k is a constant proportional to the roots of $J^c(\gamma\rho)=o$.

By making $a=o$, we return to case II, which can therefore be considered as a particular case of that discussed in III.

Lines of Equal Intensity about the Point of Intersection of Fraunhofer's Diffraction Bands.

By

H. Nagaoka, *Rigakuhakushi.*

The lines of zero intensity in diffraction figures are not sharply defined, but appear as bands. Where two such lines cross one another, the adjacent parts are usually dark, whether the light be monochromatic or not. To obtain good coincidence between experiment and calculation it will be advisable to investigate the shape of the dark curves about the intersecting bands.

When there are two systems of bands in Fraunhofer's diffraction phenomena, the intensity of light in the focal plane of the observing telescope is generally expressed by the square of the product of two functions, the evanescence of which gives rise to separate systems of bands. Denote these functions by φ and ψ, which may be considered as functions of coordinates x and y, referred to axes fixed in the focal plane. The intensity of light at any point x, y, will be

$$I = f(x, y) = \varphi^2 . \psi^2$$

The intensity at an adjacent point $x+\xi, y+\eta$ will be

$$\begin{aligned} I + \delta I &= f(x+\xi, y+\eta) \\ &= f(x, y) + \left(\frac{\partial f}{\partial x}\xi + \frac{\partial f}{\partial y}\eta\right) + \frac{1}{2}\left(\frac{\partial^2 f}{\partial x^2}\xi^2 + 2\frac{\partial^2 f}{\partial x \partial y}\xi\eta + \frac{\partial^2 f}{\partial y^2}\eta^2\right) \\ &\quad + \dots\dots\dots\dots\dots\dots , \end{aligned}$$

or

$$\delta I = \frac{\partial I}{\partial x}\xi + \frac{\partial I}{\partial y}\eta + \frac{1}{2}\left(\frac{\partial^2 I}{\partial x^2}\xi^2 + 2\frac{\partial^2 I}{\partial x \partial y}\xi\eta + \frac{\partial^2 I}{\partial y^2}\eta^2\right) + \ldots\ldots\ldots$$

The problem is to find the locus of points where the intensity will have a constant value δI near the point of intersection of the bands, which evidently is given by the equations

$$\varphi = o \quad , \quad \psi = o$$

Putting $\delta I =$ a given quantity, the equation to the curve of equal intensity will be found by using the following values of $\frac{\partial^{m+n} I}{\partial x^m \partial y^n}$ at point $\varphi = o$, $\psi = o$.

$$\frac{\partial I}{\partial x} = o \ , \qquad \frac{\partial I}{\partial y} = o \ ,$$

$$\frac{\partial^2 I}{\partial x^2} = o \ , \quad \frac{\partial^2 I}{\partial y^2} = o \ , \quad \frac{\partial^2 I}{\partial x \partial y} = o \ ,$$

$$\frac{\partial^3 I}{\partial x^3} = o \ , \quad \frac{\partial^3 I}{\partial y^3} = o \ , \quad \frac{\partial^3 I}{\partial x^2 \partial y} = o \ , \quad \frac{\partial^3 I}{\partial x \partial y^2} = o \ ,$$

$$\frac{\partial^4 I}{\partial x^4} = 24\left(\frac{\partial \varphi}{\partial x}\right)^2\left(\frac{\partial \psi}{\partial x}\right)^2 \ ,$$

$$\frac{\partial^4 I}{\partial x^3 \partial y} = 12\left(\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial y} + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial x}\right)\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial x} \ ,$$

$$\frac{\partial^4 I}{\partial x^2 \partial y^2} = 4\left[\left(\frac{\partial \varphi}{\partial y}\right)^2\left(\frac{\partial \psi}{\partial x}\right)^2 + \left(\frac{\partial \psi}{\partial y}\right)^2\left(\frac{\partial \varphi}{\partial x}\right)^2 + 4\frac{\partial \varphi}{\partial x}\frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial x}\frac{\partial \psi}{\partial y}\right] \ ,$$

$$\frac{\partial^4 I}{\partial x \partial y^3} = 12\left(\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial y} + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial x}\right)\frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial y} \ ,$$

$$\frac{\partial^4 I}{\partial y^4} = 24\left(\frac{\partial \varphi}{\partial y}\right)^2\left(\frac{\partial \psi}{\partial y}\right)^2$$

Neglecting powers of ξ, η, higher than the 4th, and putting in the values of the differential coefficients found above in the expression for ∂I, we find

$$\partial I = \left(\frac{\partial \varphi}{\partial x}\right)^2 \left(\frac{\partial \psi}{\partial x}\right)^2 \xi^4 + 2\left(\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial y} + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial x}\right)\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial x}\xi^3\eta$$

$$+ \left[\left(\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial y} + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial x}\right)^2 + 2\frac{\partial \varphi}{\partial x}\frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial x}\frac{\partial \psi}{\partial y}\right]\xi^2\eta^2$$

$$+ 2\left(\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial y} + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial x}\right)\frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial y}\xi\eta^3 + \left(\frac{\partial \varphi}{\partial y}\right)^2\left(\frac{\partial \psi}{\partial y}\right)^2\eta^4$$

$$= \left[\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial x}\xi^2 + \left(\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial y} + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial x}\right)^2\xi\eta + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial y}\eta^2\right]^2$$

Thus, the equation to the locus of equal intensity ∂I becomes

$$\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial x}\xi^2 + \left(\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial y} + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial x}\right)\xi\eta + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial y}\eta^2 = \pm\sqrt{\partial I},$$

which represents two central conics.

Referred to principal axes, the equation to the curve is transformed into

$$(A-B)\xi'^2 + (A+B)\eta'^2 = \pm\sqrt{4\partial I} = \pm C.$$

where

$$A = \frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial x} + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial y}$$

$$B = \sqrt{\left[\left(\frac{\partial \varphi}{\partial x}\right)^2 + \left(\frac{\partial \varphi}{\partial y}\right)^2\right]\left[\left(\frac{\partial \psi}{\partial x}\right)^2 + \left(\frac{\partial \psi}{\partial y}\right)^2\right]}$$

$$= \sqrt{\left(\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial x} + \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial y}\right)^2 + \left(\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial y} - \frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial x}\right)^2}.$$

Thus, B is always greater than $\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial x}+\frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial y}$, or $B>A$; hence the coefficient of ξ'^2 is always negative. The curves of equal intensity δI near the point of intersection of dark bands are, therefore two hyperbolæ, one of which is conjugate to the other. The lengths of the principal semi-axes a, b, are given by

$$a=\sqrt{\frac{C}{B-A}} \quad , \quad b=\sqrt{\frac{C}{A+B}} \ .$$

The angle ϑ made by ξ' axis with ξ axis is given by

$$\cos 2\vartheta = \frac{\frac{\partial \varphi}{\partial x}\frac{\partial \psi}{\partial x}-\frac{\partial \varphi}{\partial y}\frac{\partial \psi}{\partial y}}{B} ,$$

which evidently is the angle made by a line bisecting the angle between the tangents to φ and ψ at the point of intersection of the bands. We can also prove that the asymptotes coincide with the tangents to φ and ψ.

From the above result, the curve of equal intensity δI near the point of intersection can be easily drawn. These curves will be of great help in studying the actual diffraction figures from those given by theory.

I here give two examples of these curves, one for a rectangular aperture, and the other for two circular holes of equal size.

Rectangular aperture.—The expression for the intensity is

$$I=c\left(\frac{\sin \alpha x}{\alpha x}\right)^2\left(\frac{\sin \beta y}{\beta y}\right)^2 ,$$

where c, α, β are constants.

Assuming $\varphi = \frac{\sin \alpha x}{\alpha x}$, $\psi = \frac{\sin \beta y}{\beta y}$, the lines of zero intensity are given by

$$x = \frac{m \pi}{\alpha} \quad , \quad y = \frac{n \pi}{\beta}$$

where m, n are integers.

The curves of equal intensity are hyperbolæ—

$$\xi \eta = \pm k. \, m n.$$

The semi-axes of the hyperbolæ are proportional to $\sqrt{m n}$. The curve of equal intensity consequently recedes from the line of zero intensity, when either m or n is increased, and at a still greater rate as m and n are simultaneously increased. Thus the bright part mostly extends along the sides of the rectangle, but very little along the diagonals.

Two circular apertures.—The intensity of the diffracted ray is given by

$$I = \left(\frac{J^1(\alpha r)}{\alpha r}\right)^2 \cos^2 \beta x$$

where $r = \sqrt{x^2 + y^2}$, when the axis of x is taken parallel to the line joining the centres.

We have here to put

$$\varphi = \frac{J^1(\alpha r)}{\alpha r} \quad , \quad \psi = \cos \beta x \ .$$

Making use of the relation

$$J^2(\alpha r) = \frac{2}{\alpha r} J^1(\alpha r) - J^0(\alpha r),$$

we get the following values of the differential coefficients at the point of intersection:—

$$\frac{\partial \varphi}{\partial x} = \frac{x_n}{r_m^2} J^\circ(\alpha r_m) \quad , \quad \frac{\partial \varphi}{\partial y} = \frac{y_m}{r_m^2} J^\circ(\alpha r_m),$$

$$\frac{\partial \psi}{\partial x} = (-1)^n \beta \quad , \quad \frac{\partial \psi}{\partial y} = o ,$$

where r_m is the *m-th* root of $J^1(\alpha r)=o$, and equal to $\sqrt{x_n^2 + y_m^2}$, and $x_n = \frac{2n+1}{2\beta}\pi$. Thus, the principal axes are proportional to

$$\frac{\alpha r_m}{\sqrt{J^\circ(\alpha r_m)\left(r_m - \frac{2n+1}{2\beta}\pi\right)}} \quad \text{and} \quad \frac{\alpha r_m}{\sqrt{J^c(\alpha r_m)\left(r_m + \frac{2n+1}{2\beta}\pi\right)}}$$

Taking the distance between the centres of the circular apertures as equal to 1.72 times the radius, and tracing the curves about the points of intersection of the bands, we find a great resemblance between the diffraction figure actually observed by Fraunhofer[1] and that deduced by calculation, which otherwise gives only straight lines and rings.[2]

There are, besides, many instances in which the introduction of the curve of equal intensity enables us to find a likeness between the observed and the calculated result, especially in those problems which are easily solvable by the application of Bridge's theorem.

The present problem can be reduced to one in geometry. Considering intensity I as z coordinate, construct a surface

$$z = f(x, y) ,$$

and cut it by a plane

$$z = \delta I .$$

1. Fraunhofer, 'Werke,' München.
2. Schwerd, 'Beugungserscheinungen,' Mannheim, 1835.

The curve thus cut out by the above plane will give the contour of the diffraction pattern. The said construction is not only applicable to the case just considered, but to all Fraunhofer's and Fresnel's diffraction phenomena.

Note on Tinfoil Grating as a Detector for Electric Waves.

By

T. Mizuno, *Rigakushi.*

Professor of Physics, Daiichi Kōtō Gakkō.

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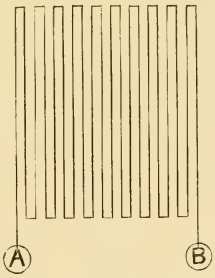
1. Much interested by Herr E. Aschkinass' experiments described in his paper read before the Physical Society of Berlin, I have been induced to repeat them. How far my results confirm his and how far they differ from them, will be seen from this note, in which I also give a few tests of the sensibility of tinfoil grating as a detector of electric waves, and an account of some experiments to determine the nature of its action.

2. I prepared my gratings by first coating a flat wooden block with tinfoil and then cutting on it a number of fine parallel slits with a sharp knife (see the annexed figure).



A and B are binding screws which are fixed in the block and facilitate the connection of the grating with a Wheatstone's bridge.

The particulars of the two gratings chiefly used in my experiments were as follows :—

(1). Rectangular in form, 3.5 c.m. by 5.1 c.m., total number of lines 97, and the resistance nearly 130 ohms.

(2). Also rectangular, 3.5 c.m. by 4.4 c.m., the number of lines 118, and the resistance nearly 232 ohms.

3. My primary vibrator was a brass cylinder 3 c.m. in diameter and 26 c.m. in length, its surface interrupted midway along its length

by a spark-gap, and its ends furnished with brass spheres 4 c.m. in diameter forming the poles. The wave-length of the electric waves produced was ascertained to be about 60 c.m. The vibrator was placed in the focal line of a wooden parabolic cylinder coated inside with tinfoil, whose height was 76 c.m., depth 21 c.m., and focal length 12 c.m. My resonator is very simple in construction and has been found very convenient in my other researches on electric waves. It is merely a rectangular strip of tinfoil, 0·8 c.m. in breadth and 60 (30 in some case) c.m. in length, with a gap in the middle, which is so fine that resonance-sparks can easily pass across.

4. I will now describe some experiments (Ex. 1.....Ex. 6) with the view of showing to what extent metallic gratings can screen the action of electric waves.

Experiment 1.

A wooden board, on which were pasted two parallel tinfoil strips, 33 c.m. in length and at a distance of 9.7 c.m. from one another, was set up vertically in front of the parabolic cylinder at a distance of about 30 c.m. from the vibrator. The grating No. 1 was brought behind the board, and after exposure for about half a minute to electric waves, its resistance was examined by a Wheatstone's bridge. The results obtained were as follows :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	129·7 ohms.	123·5 ohms.	6·2 ohms.
2	129·7 „	123·4 „	6·3 „
3	129·9 „	123·6 „	6·3 „

As Herr Aschkinass mentions, the resistance of the grating once diminished by the action of electric waves could be restored almost

to its original value by tapping it. In this experiment, resonance sparks could be discovered behind the board by means of my tinfoil resonator.

Experiment 2.

Next, a third strip was pasted on the board, half way between the other two and the experiment repeated. The results were :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	129·7	123·7	6·0
2	129·8	123·8	6·0
3	130·0	123·5	6·5

Here, the resonance sparks behind the board were very feeble.

Experiment 3.

Two more strips were then added bisecting the spaces between those in the experiment 2.

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	129·8	125·8	4·0
2	129·8	125·6	4·2
3	130·1	125·7	4·4

The resonator behind the board gave no sparks in this case.

Experiment 4.

Next, a grating, rectangular in form, 27 c.m. in length and 22 c.m. in breadth, was made, the average distance between two consecutive strips being about 0·6 c.m. Placing this grating in a

vertical position in front of the parabola and bringing the grating just behind it, the following changes in resistance were observed :

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	129·7	123·7	6·0
2	129·1	124·1	5·0
3	129·2	123·5	5·7

Experiment 5.

Substituting for the above grating a large wire grating, 1·7 m. in the side and with consecutive wires 3 c.m. apart, I have found the changes of resistance as follows :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	129·9	126·5	3·4 ‖
2	129·9	123·4	6·5 ⊥
3	129·9	126·7	3·2 ‖
4	130·2	124·5	5·7 ⊥
5	130·4	127·0	3·4 ‖
6	130·3	124·1	6·2 ⊥

The signs in the last column of the above table denote the orientations of the wire grating according as the wires were placed parallel or perpendicular to the primary vibrator. The results show how different are the effects of polarised waves on my tinfoil grating. The experiments have shewn also how sensitive the tinfoil grating is to the action of electric waves in comparison with my rectilinear tinfoil resonator, because I have found that whereas the former has shewn a large amount of change in resistance the latter gave no perceptible resonance spark.

Experiment 6.

I now placed my tinfoil grating within a glass bell-jar which was covered with tinfoil strips. I found that even in this case the change of resistance was distinctly perceptible. Thus :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	129·7	125·0	4·7
2	129·9	125·7	4·2
3	129·9	125·6	4·3

This result may be taken to indicate how imperfect would be the protection of an ordinary metallic gauze against powerful electric oscillations.

Experiment 7.

A circular copper plate 30 c.m. in diameter was vertically suspended in front of the vibrator. My tinfoil grating placed behind the plate at a distance of about 12 c.m. from it, shewed the following changes in resistance :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	129·1	121·0	8·1
2	129·3	122·3	7·0
3	129·4	122·0	7·4

Next, the distance between the plate and the grating was diminished to 2·5 c.m. The changes were as follows :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	129·3	123·0	6·3
2	129·0	123·2	5·8
3	129·5	123·0	6·5

The difference between the results of this and those of the last experiment I am inclined to ascribe to the diffraction effects of electric waves caused by the plate.

Experiment 8.

A rectangular wooden board, 69 c.m. in length and 14 c.m. in breadth, was coated all over with tinfoil. When it was held vertically with the longer edges parallel to the primary oscillations, the resistance of my tinfoil grating placed behind it shewed no change, but when the edges were placed perpendicular to the primary oscillations, I found :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	130·0	127·0	3·0
2	130·8	127·7	3·1
3	131·4	127·8	3·6

This shows that the intensity of the diffraction effect depends on the extension of the tinfoil board with respect to the direction of the primary oscillations.

Experiment 9.

A parabolic cylinder exactly similar to the one mentioned before was placed against the latter, at a distance of about 1·5 m. So that

their focal lines should be parallel. My tinfoil grating No. 2 was held in the focal line of the second parabolic cylinder and tested; thus :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	229·9	219·0	10·9
2	229·9	219·7	10·2
3	229·9	219·6	10·3

Taking away the cylinder, I found :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	230·0	227·6	2·4
2	230·0	228·0	2·0

Experiment 10.

In this experiment, my tinfoil grating No. 2 was placed just in front of a metallic plate, that is to say, near the node of the stationary electric waves produced by the plate, with the following results :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	222·0	200·0	22·0
2	227·0	206·0	21·0
3	228·0	206·5	21·5

Taking away the plate, I found :—

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	227·2	184·7	42·5
2	225·7	184·5	41·2

Experiment 11.

In order to examine whether the orientation of the tinfoil grating with respect to the primary oscillations has an influence or none on the change of its resistance, the following observations were carried out.

(1). With the grating No. 1.

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	132·4	125·0	7·4 ⊥
2	132·2	125·5	6·7 ‖
3	132·4	125·2	7·2 ⊥
4	132·4	126·4	6·0 ‖
5	132·5	125·5	7·0 ⊥
6	132·7	126·5	6·2 ‖

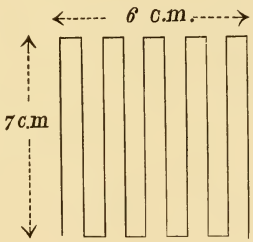
(2). With the grating No. 2.

Experiment.	Initial resistance.	Final resistance.	Decrease of resistance.
1	232·0	189·9	42·1 ⊥
2	232·0	193·0	39·0 ‖
3	232·0	187·0	45·0 ⊥
4	232·0	196·0	36·0 ‖
5	232·4	183·2	49·2 ⊥
6	232·2	194·5	37·7 ‖

The signs in the last column indicate the direction of the tinfoil strips of the gratings with respect to that of the primary oscillations. Thus, the answer may be taken as positive.

Experiment 12.

Lastly I performed some experiments to decide the question whether the change of resistance under consideration is a molecular change as in a selenium cell or simply a mechanical one. For this purpose I prepared very carefully another tinfoil grating with a much wider space between the strips. It was rectangular, 7 c.m. in length and 6 c.m. in breadth, the total number of fine strips being 51. (See the figure).



The resistance of the grating thus prepared was 209 ohms.

Now exposing this grating to the action of electric waves, I did not find the least sign of change in its resistance, except a very small one due perhaps to the heating effect. The experiment was of course tried several times and also on different occasions, but never with positive result. Here I wish also to notice that although I tried the experiment with fine German-silver wire and also fine iron wire gratings, I could never find any decided effect due to the action of electric waves on them.

Conclusions.

I. It is certain that the change of resistance of the tinfoil grating is due to the action of electric waves. So far as the electric

discharges in the primary spark-gap are oscillatory, they have an effect on the grating, but if not oscillatory, none.

II. Inasmuch as where my rectilinear tinfoil resonator fails the tinfoil grating shows the presence of electric waves, the latter must be regarded as far more efficient than the former as a detector of electric waves. Even a single spark, if oscillatory, is sufficient to produce a large effect on the grating. I would here call attention to the fact that the change in resistance of one and the same grating observed on different days during the course of my research differed in amount. This is certainly due to the conditions of the spark-gap, and consequently the intensity of the primary oscillations, and also somewhat to the time of exposure.

III. The sensibility of gratings may, up to certain limits, be increased by increasing the fineness and closeness of the strips. For, of my two gratings which are nearly equal in their dimensions but greatly different in the number of strips, the first gave the maximum change of about 6 %, while the second gave about 19 %.

IV. The phenomenon under consideration may not be molecular, and so far as my experiments go, seems to be purely mechanical. Slits cut in tinfoil with a knife, however sharp they may be, surely have margins which are zigzag. I imagine that the action of electric waves may consist in giving impulses to several strips of tinfoil so as to let the leaflets on the margins come in contact with one another and thus cause a diminution of the total resistance of the grating. Especially the fact that the spacing of the strips should have so large an influence as to reduce the effect almost to nothing seems to me to favour the above supposition. Also the fact that the change of resistance depends upon the orientation of the strips seems to point in the same direction. Still another fact which is equally important from the above point of view is that the resistance of the tinfoil

grating once diminished by an exposure to the action of electric waves can be restored nearly to the original value by tapping the grating. It may be pointed out that Prof. Minchin's experiment* on the action of electromagnetic radiation on films containing metallic powders may stand in close connection with the present subject.

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* Phil. Mag. p. 90. 1894.

The Thermo-electric Effects of Longitudinal Stress in Iron.

By

K. Tsuruta, *Rigakushi.*

Assist. Prof. of Physics, Science College,

Imperial University.

With Plates I—III.

§ 1. The foundation of our knowledge of the thermo-electric effects of stresses in iron and other metals was laid by Lord Kelvin, who in his Bakerian Lecture of 1856 on "THERMO-DYNAMIC QUALITIES OF METALS"[1] made it generally known that metals subjected to stresses, temporarily or otherwise, are thermo-electrically different from those which are not so affected. Another fact, which was established, is that "in general, metals subjected to stresses not equal in all directions will acquire the crystalline characteristic of having different qualities, as regards thermo-electricity, in different directions." These facts were demonstrated by various experiments which are described in § 105–133 of his paper.

§ 2. A distinct step of progress in the study of the subject was made through the work of Dr. Cohn[2] and of Prof. Ewing.[3] We owe to them the discovery that in iron, which shows the thermo-electric effects of longitudinal tension in a very striking manner, there is an

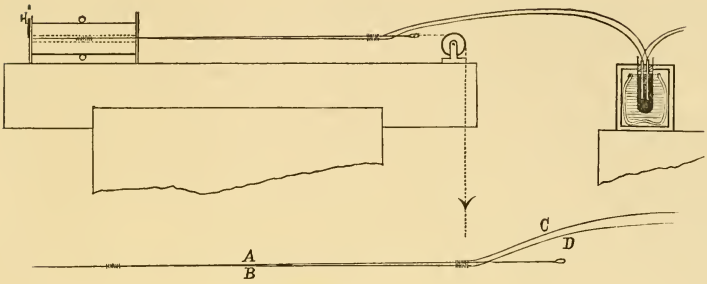
(1) Math. and Phys. Papers, vol. 2. Art. XI.
(2) Wied. Annalen. Bd. VI.
(3) Phil. Transactions. 1886.

apparent lagging of the change of the thermo-electric *E. M. F.* behind the change of the stress. When a piece of iron after being annealed is stretched beyond its limit of elasticity and by being alternately loaded and unloaded is brought to show a cyclic state, the thermo-electric *E. M. F.* changes, during the application of the load, from a value generally positive towards a value generally negative and, after passing through a minimum value, goes on towards, or tends to take, a positive value again, while, during the removal of the load, it undergoes a similar succession of changes in the reverse order, and in a way different from that during the application. Thus arises a great difference between the "on" and "off" branches of the curve showing the relation of the thermo-electric *E. M. F.* to load. For the sake of convenience and brevity in referring to this conspicuous feature, Prof. Ewing proposed to apply the term HYSTERESIS and to call the phenomenon the THERMO-ELECTRIC HYSTERESIS (with respect to longitudinal tension).

§ 3. To this subject I have since 1891 myself paid attention, and I now propose to describe my own observations about these thermo-electric effects of longitudinal tension in iron. They are by no means altogether novel; in fact, they contain little, if any, more than general confirmation and illustrations of the results obtained by others, especially by Prof. Ewing.

§ 4. I will begin by giving some details of my arrangement, which may be said to stand between those of Dr. Cohn and Prof. Ewing.

A piece of annealed soft iron wire about 1 metre long (call it wire *A*) is stretched over a very stout long block of wood mounted horizontally on a stone pier. At one end of the block there is fixed a strong cylindrical heating apparatus, which has an axial hollow space. This space is shut in at one end by a small brass piece with a hole sufficient to



allow the wire under test to pass. Passing through the hole, the wire is bent at right angles and clamped by means of a screw against the end-plate of the heating apparatus. At the middle of the apparatus there is an outlet and an inlet for steam, which is led by glass tubes from a large boiler and away to a water tank. Another piece of wire (call it wire *B*) slightly shorter than *A* is placed alongside of, and coupled with, the wire *A* by being tied together at one point with fine annealed iron wire as firmly as possible. This forms the hot junction and is put inside the axial hollow space. The other end of the piece *A* is formed into a loop, to which is tied a rope for leaden weights (each 1 kilo. in mass) hung on with the help of a small pulley. Near the loop, the wire *B* is coupled in the same way with a third piece of wire about 1 metre in length (call it wire *C*). The free end of the wire *A* is again in the same way coupled with a fourth piece of wire (call it wire *D*), exactly similar to the wire *C*. The other extremities of *C* and *D* are joined to the leading copper wires, the junctions being dipped in mercury contained in two small glass tubes, themselves surrounded by mercury contained in a large test tube. To keep the temperatures of the junctions as uniform as possible, they were still further protected by a large mass of water, and finally put in a wooden box, shut in on all sides except for two small entrance holes for the

leading wires. The wires, excepting *A*, were all wrapped in thin Japanese paper and thus insulated from each other.

§ 5. A reversing key introduced into the circuit, is necessary for eliminating not only errors caused by the variation of the zero of the galvanometer, but also any extraneous current found to accompany the one which is to be measured. The choice of the form of key to be used in connection with the present investigation was found to be one of the most difficult things to do ; indeed, this kept me from getting good results for a long time. Many forms were tried, and the rocker of the usual construction together with six mercury pools in a block of wood found to be the best of them all. My rocker was made of copper and was very small. Great care is of course to be taken not to expose the key to any considerable source of heat ; and in my own case the whole reversing arrangement was put within a wooden box and moved by means of a handle from without.

§ 6. As I had to deal with a very feeble current, the galvanometer, which was of low resistance (0·26 ohms.), had to be made highly sensitive and to be also well damped. The adjustment of a controlling magnet, or two magnets in case of need, caused a good deal of trouble and loss of time in every experiment. At the same time, as a high degree of sensitiveness was attained, any small causes of disturbance became proportionally pronounced and a series of readings would come out somewhat irregular. I, therefore, usually did not push the sensibility to a very high degree, but was content if it was quite sufficient to show the variation of the thermo-electric *E. M. F.* No reduction of readings taken to absolute measures was made, as the aim of the present series of experiments was simply to study the general nature of the thermo-electric hysteresis.

§ 7. The curves showing the relation of the thermo-electric *E. M. F.* to load, which I obtained in my earlier experiments on an-

nealed soft iron, were all of the type given by Dr. Cohn, and can be represented by Fig. 3 or 4, Pl. I. Being at the time unacquainted with Prof. Ewing's paper, it cost me much labour to establish the fact that to get a curve of Prof. Ewing's type, which can be represented by Fig. 6, Pl. I., it is necessary to pull the annealed soft iron wire beyond its limit of elasticity. This, however, led me to trace the manner of transformation of the thermo-electric curve, as the range of loading and unloading is progressively extended up to and beyond the limit of elasticity.

§ 8. To illustrate the subject of the last paragraph, one of my experiments may be here cited. The object being sooner attained with a thinner piece of wire, one of soft iron 0·64 m.m. in diameter was tested. It was carefully annealed in the air with Bunsen flame three times,—twice with a weight which served the purpose of making the wire straight and finally once after the weight had been removed. The results obtained with the above wire are given in the following tables, which are also graphically represented in Figs. 1–6, Pl. I. The cycles of loading and unloading were in the order: (1) 0 — 3 — 0, (2) 0 — 6 — 0, (3) 0 — 8 — 0, (4) 0 — 10 — 0. The leaden weights by means of which longitudinal tension was applied to the wire were, as before mentioned, each one kilogramme in mass. Each cycle was gone through twice, for I considered that the readings in the second would be nearer than those in the first to the perfectly cyclic state of changes for the range of loading and unloading. The cycles ought to be represented by one continuous curve, yet to avoid confusion, they are so grouped that one of the pair in each figure refers to the second process of loading and unloading, while the other corresponds to the next consecutive cycle in which the range of loading was extended (the former in full lines and the latter in dotted lines). The curves are all drawn after Prof. Ewing, that is to say, the horizontal axis is the axis of

loading and unloading, and the vertical axis that of *E. M. F.*, considered as positive in the sense of from below upwards.

The iron wire was found initially to give a current from the part affected to the part unaffected through the hot junction : the representative point has accordingly a positive ordinate (Fig. 1). On being loaded, the *E. M. F.* was so reduced that, even under the load of 3 kilos., the representative point passes over far below the axis of load. On being unloaded, the *E. M. F.* assumed a still more negative value, and passing through a minimum, it showed a tendency to turn back towards the positive side, though never attaining its initial magnitude. The second process of loading and unloading gave a curve which

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	+ 8.0	6	−38.4	0	−66.7	2	−65.2
1	− 0.5	5	−45.5	1	−62.5	3	−62.8
2	−23.6	4	−55.5	2	−61.8	4	−57.7
3	−38.8	3	−60.3	3	−58.0	5	−49.5
2	−43.4	2	−68.0	4	−54.0	6	−44.0
1	.....	1	−67.2	5	−44.1	7	−36.0
0	−37.5	0	−62.0	6	−41.8	8	−28.5
1	−37.0	1	−56.8	7	−34.7	7	−35.0
2	−38.8	2	−58.0	8	−28.0	6	−47.0
3	−39.5	3	−56.5	7	−37.5	5	−56.0
2	−45.6	4	−52.0	6	−44.0	4	−62.0
1	−46.5	5	−47.0	5	−53.2	3	−68.0
0	−41.1	6	−40.0	4	−62.0	2	−73.5
1	−38.9	5	−49.1	3	−71.0	1	−75.5
2	−39.2	4	−57.5	2	−74.5	0	−69.5
3	−39.5	3	−63.1	1	−76.2		
4	−42.1	2	−69.0	0	−70.3		
5	−42.8	1	−70.0	1	−66.0		

encloses a small area. The "on" branch of the curve shows a very little fluctuation, but, if anything can be seen from it, the manner of variation is certainly of like nature to the corresponding branch of the first process.

The range of loading and unloading was then extended to 6 kilos. (Fig. 2). The "on" branch is more or less sinuous, and the "off" branch runs towards a more negative region, having as before a minimum near the close of unloading. By a cyclic change of load-

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	−69.5	1	−66.4	2	−65.7	2	+11.1
1	−67.5	2	−65.5	3	−63.5	3	+ 3.5
2	−65.0	3	−61.0	4	−58.5	4	−12.5
3	−61.9	4	−57.7	5	−53.2	5	−26.5
4	−58.0	5	−52.0	6	−46.5	6	−39.0
5	−50.0	6	−45.0	7	−39.0	7	−46.2
6	−44.8	7	−36.0	8	−30.8	8	−46.0
7	−36.0	8	−30.0	9	−21.5	9	−45.3
8	−29.5	9	−20.0	10	−13.5	10	−38.5
9	−20.9	10	−13.0	10	−16.5	9	−50.0
10	−14.0	9	−21.1	9	−31.0	8	−58.0
9	−19.0	8	−29.1	8	−39.0	7	−67.8
8	−30.0	7	−39.0	7	−52.0	6	−77.2
7	−38.0	6	−48.0	6	−59.5	5	−79.0
6	−47.0	5	−55.5	5	−65.0	4	−76.0
5	−56.0	4	−63.5	4	−63.0	3	−66.5
4	−63.0	3	−69.0	3	−46.0	2	−51.8
3	−69.0	2	−77.0	2	−34.0	1	−28.2
2	−75.0	1	−77.0	1	−10.0	0	− 7.9
1	−77.0	0	−74.0	0	+ 6.6		
0	−72.5	1	−68.5	1	+13.5		

ing and unloading gone through once more, there is brought forth the form of the curve which is of the type given by Dr. Cohn. A further extension of the range of cyclic change by 2 kilos., making the greatest load 8 kilos., wrought no change in the form of the curve ; it had only the effect of prolonging the branches towards the positive region of *E. M. F.*

Another extension of the range up to 10 kilos. had the same effect, and here the two cyclic curves, the dotted and the full, are almost coincident with each other, this in the preceding stages not being the case to such an extent. With 10 kilos. the wire was loaded to the utmost, for when I added only 0·2 kilos., I observed a large strain which threatened to break down the wire. So I took away the added load and obtained the reading corresponding to 10 kilos. This is the reason why the dotted curve in Fig. 5 is not here connected. This permanent drawing of the wire wrought a great change in the variation of *E. M. F.* : for when the wire was unloaded down to 5 kilos., further unloading resulted in bringing the representative point back towards the positive side of the axis of load and finally up to the initial position.

The cycle (0—10—0) gone through immediately after this great change is shown in Fig. 6., Pl. I. It is exactly of the type given by Prof. Ewing. Experiments with other pieces of wire showed that once the change had set in, the cyclic curves obtained after the lapse of hours and days were all exactly of the above type.

§ 9. The above experiment made, as it was, upon a single sample of soft iron, must be regarded as a particular example. In fact, the curves obtained, even with pieces of wire cut from the same bundle, showed some differences in details. So far, however, as my experiments go, all samples of soft iron well annealed, when tested, agree in exhibiting a considerable reduction of *E. M. F.* on being

loaded for the first time, in exhibiting a gradual transferrence of the curves, as a whole, towards the negative side of the axis of load, at the same time an upward extension of the branches corresponding to greater loads, and, lastly, in exhibiting a great change, as above described, when permanent drawing sets in.

A description of the features of the thermo-electric curve arrived at in the above manner is rendered useless by very full comments on them by Prof. Ewing.[1]

§ 10. I will now go on to describe my own observations on the effects of loading and unloading at different stages of the thermo-electric curve.[2] Even when the process of loading and unloading is performed within a certain limited range, not exceeding the uppermost limit of the main cycle, the thermo-electric hysteresis manifests itself by causing the "off" branch to lie quite clear of the "on" branch. The curves, closed or otherwise, formed in this way will be called minor cyclic curves.

One of my experiments, given in the following table, made on soft iron wire 0·54 m.m. in diameter, may be cited as illustration. For the sake of clearness, the minor cyclic curves are represented separately in Figs. 7, 8, 9, and 10 Pl. II, with the main cycle for comparison. They were so chosen as to correspond respectively to the distinct stages of the "on" branch. The first cycle (0—1—0) which lies quite below the maximum is found to enclose a very small area if any. Once the maximum point is passed, as in the second cycle (0—3—0), the "on" and "off" branches begin to enclose a considerable area, and to show the characteristic features of the cyclic curve, which will be seen quite fully developed in the third minor cycle (0—6—0).

(1) l. c., § 8–11.
(2) l. c., § 12.

To obtain minor cyclic curves on the "off" branch of the main, the following observations were made on the same wire. This and

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	+42.0	8	−60.3	0	+37.5	4	+16.0
1	+50.3	7	−70.8	0.5	+42.0	5	− 5.5
2	+52.5	6	−73.0	1	+46.2	6	−26.5
3	+41.0	5	−70.5	0.5	+41.0	5	−32.8
4	+21.5	4	− 64.0	0	+37.0	4	−35.6
5	+ 0.3	3	−35.0	1	+45.5	3	−25.0
6	−19.8	2	−10.0	2	+44.0	2	−11.0
7	−33.3	1	+19.5	3	+32.5	1	+11.7
8	−35 5	0	+37.0	2	+29.2	0	+31.5
9	−36.5			1	+27.5		
10	−29.0	0	+36.3	0	+35.0		
11	−23.8	0.5	+45.0	1	+43.5		
10	−36.0	1	+45.2	2	+40.5		
9	−48.0	0.5	+41.8	3	+33.8		

the above experiments were carried out on different days, so that they are not to be combined into a series.

We have here three minor cycles (8−11−8), (4−11−4), and (1−6−1), which are shown in Fig. 11, Pl. II. They are, again, so chosen as to correspond to the distinct stages on the "off" branch, one on the right and two on the left of the minimum point. In the first cycle, again the effect of the hysteresis seems to be very small, it being borne in mind that the readings taken were always such that there were as many which gave representative points lying on one side as of those which gave points lying on the other side of the almost straight mean courses of the curve. The cycle (1−6−1) has exactly the same features as the one (0−6−0), Fig. 10, on the "on" branch,

the only difference being that the former lies above, and the latter below the respective branches of the main cyclic curve. The minor cycle

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	+38.5	8	−106.2	8	− 90.0	2	+ 9.0
1	+41.7	9	− 80.0	9	− 85.0	3	+ 6.0
2	+42.5	10	− 69.5	10	− 69.0	4	− 8.5
3	+31.7	11	− 54.5	11	− 55.0	5	−38.0
4	+ 7.0	10	− 73.0	10	− 75.2	6	−66.0
5	−23.0	9	− 85.0	9	− 88.0	5	−83.0
6	−54.0	8	−107.5	8	−108.5	4	−68.0
7	−74.8	7	−123.0	7	−125.0	3	−57.0
8	−80.0	6	−135.0	6	−135.0	2	−35.0
9	−76.0	5	−129.5	5	−128.8	1	− 9.5
10	−66.0	4	−111.0	4	−114.5	0	+27.0
11	−52.0	5	− 98.0	3	− 87.8		
10	−68.0	6	− 93.0	2	− 40.5		
9	−85.0	7	− 92.5	1	− 10.5		

(4−11−4) refers to the stage in which the minimum point has just been passed. The "on" branch has apparently a point of inflexion, and the "off" coincides with the corresponding portion of the main cyclic curve. It is thus intermediate in form between the two preceding minor cyclic curves, and reminds us of one of the forms through which the main cyclic curve was evolved, as explained in § 8 (See Fig. 3 and 4, Pl. I).

§ 11. These experiments suggest that in the thermo-electric curve the effect of the hysteresis is more conspicuous in the region between the axis of zero load and the minimum points, than in the region beyond them. In the latter, the iron seems to have been brought into a stable condition, inasmuch as when tension is applied

and then removed or vice versâ, the thermo-electric *E. M. F.* goes through almost the same series of values.

§ 12. The next group of my experiments relates to the effects of agitation, which, as was shown first by Prof. Ewing,[1] are very strikingly manifested in largely destroying the effect of the hysteresis. As an instance, take the following experiment on annealed iron wire 0·54 m.m. in diameter :—

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	+21.5	6	−23.0	9	−41.8	(tapped)	−22.0
1	+31.0	7	−30.0	8	−48.6	2	−17.0
2	+31.5	8	−30.7	7	−58.0	1	− 2.4
3	+19.5	9	−35.5	6	−59.8	0	+15.3
(tapped)	+ 8.5	10	−29.0	5	−62.0		
4	+ 9.0	11	−23.5	4	−53.0		
5	− 9.5	10	−30.2	3	−38.5		

Loaded up to 3 kilos., the wire was agitated by briskly tapping with a piece of wood the string over the pulley by means of which the weights were hung on. The reading which was about 20 divisions before agitation was found to be reduced after it to only about 9 divisions. When on the "off" branch the wire was under the same load, I again tapped it and found the reading of about 39 divisions reduced to about 22. See Fig. 12, Pl. II.

§ 13. The wire was, then, agitated each time it was loaded or unloaded and carried through the same cycle of loading and unloading (0−11−0). The readings taken were as follows :—

(1) l. c., § 14.

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	+13.5	6	−33.0	10	−33.0	4	−35.5
1	+12.6	7	−38.2	9	−38.0	3	−22.5
2	+ 6.0	8	−36.5	8	−42.0	2	+11.3
3	+ 7.0	9	−33.2	7	−43.0	1	+22.0
4	− 9.0	10	−34.0	6	.....	0	+25.0
5	−23.5	11	−27.5	5	−45.0		

Examining the curve (the dotted one in Fig. 13, Pl. II) in which the result is represented, we see that the maximum point on the "on" branch becomes now barely recognisable, and that the "off" branch does not go up so straight as usual. The two branches are not only still separated, but also cross each other in such a way that the "off" branch which is for greater loads below the "on," comes out above it for smaller loads.

Immediately after the above experiment, another cycle (0−11−0) was gone through without agitation, and the following readings were obtained :—

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	+26.5	6	−26.0	10	−29.0	4	−52.0
1	+30.8	7	−30.5	9	−37.7	3	−27.2
2	+17.5	8	−30.2	8	−45.4	2	−16.0
3	.....	9	−26.0	7	−53.0	1	+ 3.0
4	+ 9.7	10	−26.0	6	−56.0	0	+19.0
5	− 4.5	11	−21.2	5	−57.0		

This result is graphically shown in connection with the above in Fig. 13, Pl. II. It is apparent that the effects of the hysteresis are immediate and very conspicuous.

§ 14. "An instructive method of studying the influence of vibration in destroying or rather in greatly reducing hysteresis, is to

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	−56.5	(tapped)	− 99.0	16	−116.0	7	−148.5
1	−50.0	8	− 97.0	15	−120.0	(tapped)	−138.7
(tapped)	−39.6	9	−108.0	14	−126.5	6	−136.5
2	−40.0	10	−117.0	13	−134.5	5	−125.5
3	−41.5	11	−123.0	12	−138.5	4	−107.0
4	−47.5	(tapped)	−130.7	11	−145.5	(tapped)	− 98.8
(tapped)	−61.5	12	−129.0	(tapped)	−144.0	3	− 93.2
5	−60.9	13	−127.0	10	−147.0	2	− 80.5
6	−71.7	14	−123.1	9	−152.0	1	− 65.5
7	−85.5	15	−120.0	8	−153.5	0	− 53.0

partially load or unload in the ordinary way, and then pausing at any stage in the process, to tap the wire."(1) The following is one of my experiments carried on according to this method, the diameter of the wire tested being 0·77 m.m. It is set forth in Fig. 14, Pl. II.

This experiment exactly verifies the results given by Prof. Ewing.(2) As he remarks, the maximum points on the portions corresponding to partial loadings in the "on" branch are quite characteristic. So also are the minimum points on the portions corresponding to partial unloadings, in the "off" branch. Beyond the minimum points of the main cyclic curve, owing perhaps to the stable conditions in which the iron now exists, these features become somewhat altered in a way apparent from the figure.

Again, it will be seen that at points lying in the region between

(1) Prof. Ewing, Exp. Reseaches in Magnetism, § 74.
(2) l. c., § 38–39.

the maximum and minimum points, agitation imparted to the wire tends to shift the representative points lower in the diagram on the "on" branch, while it is just the opposite on the "off" branch. Below and up to the maximum point on the "on" branch the representative points are shifted upwards, and beyond the minimum points on the two branches shifted downwards though to very small extents. If the effect of agitation is solely to shake out the traces of hysteresis, then such an experiment as the above can be regarded as one which would contribute much towards the understanding of the nature of the hysteresis itself.

§ 15. The above experiment was varied in such a way that throughout either "on" or "off" branch the wire was kept undisturbed or tapped, while throughout the other branch tapped or kept undisturbed. The results, obtained with a piece of wire cut from the same bundle as above but with quite a different experimental arrangement, are shown in Fig. 15, Pl. III, in which the curves for undisturbed conditions are drawn in full lines and those for agitated conditions in dotted lines. An inspection of the figure will show that the full "off" branch, when taken in conjunction with the full "on," would make up a complete cyclic curve obtained in the usual way, while the dotted "on" with the dotted "off" make up a complete cyclic curve obtainable by continually tapping the wire.

In the above experiment the order of the processes gone through is that indicated in the figure by arrow heads. Experiments made specially showed that the general character of the curves is independent of the order, that is to say, we obtain the same results when we go through, first the "on" branch without agitation, next the "off" with it, then the "on" again with it, and lastly the "off" without it. This is consistent with the result at the end of § 13.

§ 16. All the foregoing experiments show very well with what

facility that which, whatever it is, mainly contributes to the production of the hysteresis, comes and goes with agitation. We cannot indeed help thinking of the thermo-electric hysteresis as due to something like molecular viscosity or constraints in iron.

§ 17. The following experiment on the same wire as in § 12 was made to complete the experiment of § 14.

After a cycle of loading and unloading had been gone through and the familiar curve obtained (not here given), the wire was tapped at a certain stage (6 kilos.) in the next process of loading, the representative point being thus shifted below (See Fig. 16., Pl. III). The wire was then unloaded down to 1 kilo. and successively loaded on again. The course of the curve is exactly the same as that we had before in the minor cyclic curves. Arriving at the uppermost limit

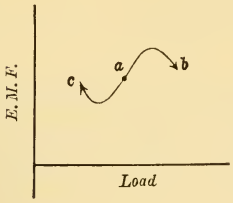
Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	+15.3	1	− 2.0	9	−44.5	6	−30.8
1	+23.2	2	+ 5.0	8	−54.0	7	−41.1
2	.....	3	+ 4.0	7	−61.0	6	−46.0
3	+15.3	4	− 4.6	6	−67.3	5	−50.3
4	+ 3.3	5	−16.5	5	−62.5	4	−44.2
5	−12.2	6	−31.5	4	−55.0	3	−36.0
6	−26.5	7	−37.0	3	−37.0	2	−17.5
(tapped)	−31.0	8	−41.5	2	−17.5	1	− 1.0
5	−44.5	9	−38.5	(tapped)	− 5.0	0	+17.0
4	−44.0	10	−35.0	3	− 4.0		
3	−30.0	11	−27.6	4	− 8.2		
2	−15.2	10	−37.2	5	−20.5		

of loading (11 kilos.), I began to unload and tapped the wire again at a certain stage (2 kilos.). The effect of hysteresis being thus

shaken out, the representative point in the diagram rose considerably. Instead of unloading as before, loading was began, continued up to 7 kilos., and then reduced to zero again. The course of the curve is here again exactly the same as that we had in the minor cyclic curves without agitation.

§ 18. An examination of all the experiments enables us to understand how the thermo-electric changes set in and go on when the wire is brought to a certain stable condition by tapping. Indeed they give us a confirmation of a remark of Prof. Ewing's,[1] which it will be well to quote here :

" The thermo-electric quality of a piece of iron which has been shaken into a condition of molecular stability changes, first, towards (say) positive, and later, towards negative, when stress is applied and increased.....And the changes have the reverse signs from those justed stated if the direction of the applied stress is reversed. Thus, let *a* be a point expressing the relation of thermo-electric *E. M. F.* to load, which is reached by tapping the metal or by exposing it to the process of demagnetising by reversals. If from this point we go on loading we have the curve *ab*. If from the same point we had began to unload we should have had the curve *ac*."

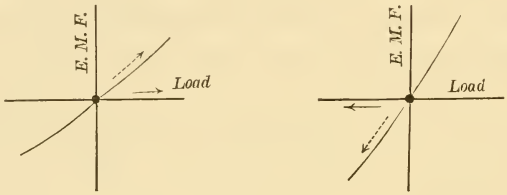


§ 19. One of the results stated by Prof. Ewing, which I could not verify in the course of my experiments, is the formation of a small loop in the cyclic curve when we turn from loading to unloading at the uppermost limit of loading. In my experiments the " off " branch usually goes nearly straight below the " on " and gets appre-

(1) l. c. § 46.

ciably clear of it after two or three steps of unloading. There were of course some readings which gave points lying above the "on" branch, but I take it to be still open to consider the formation of the loop as one of the distinct features in the thermo-electric curve.

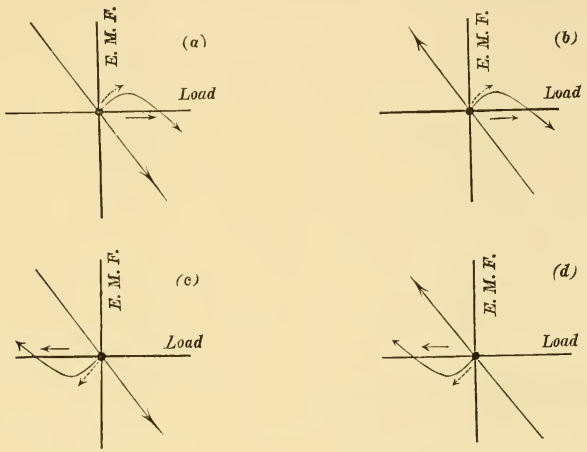
§ 20. I have remarked that the points of the thermo-electric curve which lie to the right of the minimum points correspond to the more stable conditions of the iron. Examining how the thermo-electric changes set in at these points when we *begin* to load or unload the wire, we have to distinguish between the two cases represented in the annexed figures. The spots in the figure are meant to be repre-



sentative points, and the sloping lines to be the limbs of the thermo-electric curve under consideration. There are added the axes of reference drawn through the spots, with respect to which the limbs lie in the first and third quadrants. Dotted arrow heads show the initial thermo-electric changes produced by loading or unloading the wire as indicated by full arrow heads. Thus, we see that the increase or decrease of the load corresponds to the increase or decrease of *E. M. F.*

§ 21. If we now examine this question on the other side of the minimum points when the metal is brought to more stable conditions by being subjected to agitation, it will be seen that *so far as only the initial changes are concerned* the same relation holds true. Of the four cases represented in the following figures, two (*a* and *c*) refer to the

states of the metal after it is tapped when we are going through the "on" branch, and the other two (*b* and *d*) when we are going through the "off" branch. The effect of agitation would be to bring

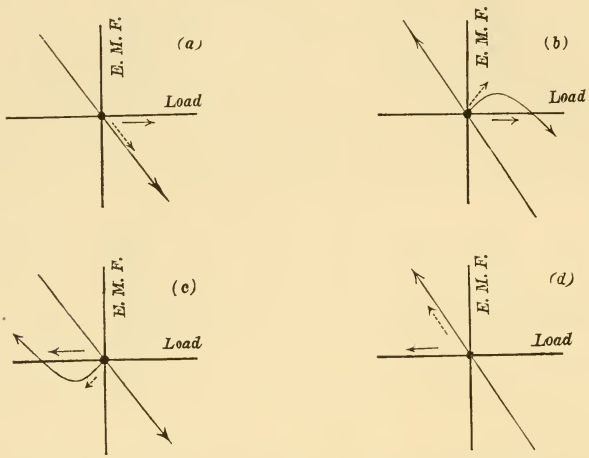


the molecules of the metal into altered configurations by making them lock into each other and come closer together, the accumulated hysteresis, if there be any, being thus shaken out. In the present case, therefore, the effect of pulling or relaxing on the change of *E. M. F.* may be considered to come out unmasked. The changes of *E. M. F.* as represented in the above figures may be regarded as the proper effects of mechanical actions upon the iron in stable conditions.

§ 22. With respect to the iron under stress and not subjected to agitation, experiments have brought forth some quite different features in the initial effects of application and removal of load. Four cases which correspond to the above enumerated are shown in the annexed figures.

The difference between this and the preceding classes consists in

that, in the latter case, agitation has had its effects before the loading or unloading takes place, while in the former case the conditions so altered remain undisturbed during the loading or unloading. The present case may, therefore, be regarded as equivalent to the preceding



case with the effects of the hysteresis added. Now pulling or relaxing the wire may probably produce to a certain extent, though not quite to the same degree, similar effects as agitation itself in shaking out the hysteresis, and moreover the effect of strengthening or loosening the molecular ties holding the molecules of the iron in a stable equilibrium under the load present. The former of these effects will carry the representative point on the "on" branch downwards (*a* and *c*), and on the "off" branch upwards (*b* and *d*). The latter effect will carry the representative point in case of pulling upwards (*a* and *b*), and in case of relaxing downwards (*c* and *d*). Therefore, in (*a*) and (*d*) the two effects conflict with each other, while in (*c*) and (*b*) they are concurrent. If we assume the former effect to be the

greatest, as it probably is, the thermo-electric curve must have its initial trends always in the sense dictated by that greatest effect.

§ 23. Besides the initial trends, I have in the above figures indicated the courses of the thermo-electric curve when the loading or unloading is further continued. It will be seen that after passing through a maximum or minimum point the curve goes over to lie again in the fourth or second quadrant. Thus, the manner of formation of the main cyclic curve is repeated, almost everywhere in the field of the diagram, although not so fully developed in some cases as in others. This must have arisen from a complex change in the mechanical constitution of the iron, arising from *the interaction of the effects of the hysteresis and stress.* It will be of course premature and quite speculative to try to make out in a precise manner what is that change and how it takes place.

§ 24. After all the previous experiments had been finished, I made some others on iron wires in the hard drawn state in which they had been purchased.[1] The general result obtained is, that although in this case the thermo-electric curves are somewhat peculiar in form, they still have almost all those features that were pointed out as characteristic in connection with annealed soft iron wires ; in fact, some features which had been formerly hard to discover are found singularly well developed in these experiments.

§ 25. Corresponding to the experiments of § 8, I have the following observations which were made on iron wires 0·7 m.m. in diameter and exceedingly soft when annealed. By trial I ascertained that wires from the same specimen in the hard drawn state could be loaded up to 36 kilos. and thus became appreciably more hardened still.

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(1) Prof. Ewing, l. c. § 42–44.

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	+22.0	4	−31.5	16	−25.0	20	+ 9.3
2	+29.7	2	−27.8	14	−40.0	22	+24.0
4	+27.0	0	−20.0	12	−53.0	24	+39.8
6	+16.0	2	−10.0	10	−61.5	22	+22.0
8	+ 3.0	4	− 3.5	8	−67.5	20	+ 7.0
10	− 8.0	6	− 3.0	6	−70.5	18	− 9.5
8	−19.3	8	− 6.0	4	−66.0	16	−24.0
6	−27.5	10	− 8.0	2	−48.5	14	−40.0
4	−31.8	12	−12.0	0	−31.0	12	−53.7
2	−27.5	14	−12.4	2	−21.0	10	−64.0
0	−15.5	16	− 8.0	4	−16.5	8	−71.5
2	− 6.0	18	− 0.2	6	−17.0	6	−70.5
4	− 3.0	20	+12.2	8	−20.0	4	−69.0
6	− 1.0	22	+24.0	10	−23.5	2	−54.5
8	− 2.8	24	+38.8	12	−24.5	0	−36.0
10	− 7.0	22	+25.5	14	−18.0		
8	−20.0	20	+ 8.0	16	−11.0		
6	−28.0	18	− 8.9	18	− 2.0		

The result is plotted in Fig. 17, Pl. III, an inspection of which is sufficient to show how the characteristic features are all reproduced here. The thermo-electric changes follow one another in a remarkably steady manner and make the representative points arrange themselves in a very well defined curve.

§ 26. Even the above experiment will enable us to foresee what can be brought out by experiments on minor cyclic curves. Therefore, I only give here one of my observations together with its graphical representations in Fig. 18 and 19, Pl. III. The wire tested was the same as in the experiment first described.

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	−28.0	6	−17.5	0	−34.7	24	+40.0
1	−21.5	7	−18.5			22	+23.5
2	−17.9	8	−20.0	0	−35.5	20	+ 8.2
3	−13.1	9	−23.3	2	−24.7	18	− 8.7
2	−19.5	10	−21.9	4	−19.0	16	−25.0
1	−23.9	9	−28.0	6	−20.2	14	−38.9
0	−28.9	8	−34.0	8	−23.5	12	−52.5
		7	−39.0	10	−26.5	10	−63.0
0	−35.0	6	−43.0	12	−25.0	8	−69.1
1	−27.0	5	−46.5	14	−20.0	6	−72.0
2	−23.5	4	−47.8	16	−11.8	4	−66.2
3	−19.5	3	−46.5	18	− 1.9	2	−55.5
4	−18.0	2	−43.2	20	+10.5	0	−34.1
5	−16.5	1	−40.9	22	+24.0		

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
14	−44.9	10	−70.3	22	+20.4	2	−63.0
16	−30.6	8	−76.0	24	+39.0	4	−50.5
18	−13.5	6	−79.8	22	+22.0	6	−43.0
20	+ 3.0	4	−74.2	20	+ 4.0	8	−39.6
22	+20.4	6	−63.3	18	−13.6	10	−37.0
24	+38.0	8	−53.0	16	−30.5	8	−50.0
22	+22.1	10	−45.2	14	−46.0	6	−59.0
20	+ 4.2	12	−37.9	12	−57.6	4	−65.8
18	−14.5	14	−29.1	10	−68.7	2	−63.0
16	−30.2	16	−19.5	8	−77.0	0	−42.0
14	−46.5	18	− 7.0	6	−81.5		
12	−59.7	20	+ 6.0	4	−74.3		

§ 27. I will now give account of some experiments on the effects of agitation on the same hard drawn wire. The first two tables which follow, together with Figs. 20 and 21, Pl. III, correspond to the experiments of § 14 and 17 respectively, and the last table together with Fig. 22 to those of § 13.

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	−34.0	(tapped)	−30.5	18	− 6.2	12	−54.0
1	−28.9	9	−26.0	20	+ 6.0	10	−65.0
(tapped)	− 3.5	10	−23.3	22	+19.5	8	−71.1
2	0	11	−25.5	24	+33.5	6	−74.5
3	+ 2.8	12	−25.3	22	+20.0	4	−66.5
4	+ 2.2	13	−25.0	20	+ 3.0	(tapped)	−50.0
5	− 1.4	14	−22.7	18	−11.5	3	−54.0
6	− 5.1	15	−19.0	16	−27.5	2	−52.7
7	−10.6	16	−16.4	14	−40.5	1	−48.5
8	−16.8	(tapped)	−18.9	(tapped)	−42.8	0	−38.5

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
0	−46.5	2	−56.3	20	+ 4.9	16	− 38.0
1	−39.1	1	−51.0	22	+22.5	18	− 17.0
(tapped)	+ 2.0	2	−41.5	24	+42.0	16	...
0	− 1.5	4	−34.0	22	+23.3	14	− 59.0
2	+11.5	6	−32.4	20	+ 4.5	12	− 78.5
4	+15.0	8	−32.5	18	−19.0	10	− 94.2
6	− 1.0	10	−34.8	16	−40.0	8	−104.5
8	−16.5	12	−37.6	14	−61.0	6	−109.0
(tapped)	−46.0	14	−33.0	12	−76.0	4	− 98.0
6	−59.0	16	−24.0	(tapped)	−73.0	2	− 54.0
4	−63.0	18	−12.9	14	−58.0	(tapped)	− 27.5

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
4	−19.0	12	−36.0	8	−79.2	0	−48.5
6	−20.0	14	−33.0	6	−85.0		
8	−32.5	12	−44.5	4	−80.0		
10	−37.2	10	−63.4	2	−67.5		

Load.	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*	*Load.*	*E. M. F.*
	With tapping	24	+37.3		Without tapping	22	+18.7
0	−11.5	22	+21.6	2	− 4.0	20	+ 1.9
2	−10.8	20	+ 2.5	4	− 1.0	18	−15.0
4	−27.6	18	−16.0	6	− 9.0	16	−30.0
6	−39.0	16	−29.5	8	−26.0	14	−44.5
8	−40.0	14	−44.2	10	−33.7	12	−59.0
10	−40.0	12	−58.0	12	−30.5	10	−70.0
12	−39.8	10	−68.0	14	−29.5	8	−84.0
14	−29.3	8	−72.0	16	−21.0	6	−80.0
16	−22.0	6	−70.0	18	−11.0	4	−76.0
18	−11.1	4	−50.0	20	+ 2.8	2	−61.0
20	+ 4.2	2	−36.6	22	+17.5	0	−41.0
22	+21.5	0	−13.0	24	+36.0		

§ 28. Next I tried a few experiments on iron wires hardened by stretching them beyond their limits of elasticity. Pieces cut from the same bundle as the foregoing, after being carefully annealed, were drawn with about 15 kilos., and coupled with each other. When tested, they showed nothing worthy of notice; the thermo-electric curves obtained were in every respect of Prof. Ewing's type. It is evident, as it is from other points of view, that by the operation of wire drawing metals are subjected to far more complex combinations of stresses and strains than when they are simply stretched.

§ 29. P. Bachmetjew[1] has made some experiments on the same subject as that of the present paper. He describes two methods of investigation, one of which is exactly the same as that used by Dr. Cohn, and the other is to make a couple of two metals and to pull or compress one of them, the thermo-electric current between the metals themselves being compensated by another similar couple. Whenever iron or nickel was coupled with other metals, such as copper, and was alone subjected to tension, the curves showing the relation of *E. M. F.* to load were found to be more or less curved, while in other cases they were almost straight.

The two methods are not essentially different, but the interest of the second method lies in its enabling us to see, at least qualitatively, the variation of the thermo-electric property of iron under longitudinal tension with respect to other metals like copper. A few experiments were tried on couples made of annealed iron wires and copper wires annealed as well as hardened ; I found again the familiar form of the thermo-electric curve.

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(1) Thermo-elektrische Untersuchungen, Repert. der Physik, Bd. XXVI. 1890.

Thermo-electric Effects of Longitudinal Tension in Different Metals.

By

K. Tsuruta, *Rigakushi.*

Assist. Prof. of Physics, Science College.

With Plate IV.

§. 30. Having investigated the general features of the phenomenon of thermo-electric hysteresis with respect to longitudinal tension in iron, I proceeded to examine it in other metals. Measurements of a comparative order had been long since amassed and now it only remained to express them in absolute measure. One of the principal things to be measured is the thermo-electric *E. M. F.* produced, and of several methods available, one of the most practical, and indeed that adopted by Prof. Ewing,[1] is to determine the constant of the galvanometer by passing through it a known and, at the same time, constant current and then to calculate the *E. M. F.* by finding the resistance of the circuit.

It was therefore necessary first to investigate how the resistance changes when the metal under test is subjected to a varying longitudinal tension. The metal, consisting of stretched and unstretched parts, together with the leading wires, was put in the fourth arm of a standard resistance box. After the resistance had been determined in

(1) Prof. Ewing, Thermo-electric Quality of iron, l. c., § 20.

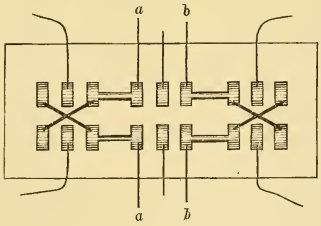
the usual way, the current in the diagonal was reversed and the resistance again determined. Since the *E. M. F.* of the thermo-electric couple is very small, amounting only to a few micro-volts, and the above two determinations of resistance do not differ much, the true value of the resistance in question is equal to the mean of the two determinations multiplied by the ratio of the resistances put in the proportional arms. As an example may be cited the following observations made on an annealed soft iron wire 0·5 m.m. in diameter :—

Load in kilos.	*Resistance in ohms.*	*Load in kilos.*	*Resistance in ohms.*
0	.....	8	3.6120
2	3.6050	6	3.6114
4	3.6078	4	3.6100
6	3.6101	2	3.6096
8	3.6105	0	3.6090
10	3.6127		

So far as my determinations went, which were made immediately after each series of measurements of the *E. M. F.*, the numerical values obtained were closely of like nature to the above. It may be that the resistance of the iron wire under varying longitudinal tension suffers a corresponding, perhaps regular, variation, but as no law of the variation is discernible from my determinations, and the amount of the variation is always quite small, I think it proper to take the resistance as constant for the purpose of the present investigation. Thus, there being no need of measuring the resistance at each step of loading or unloading the wire, both observations and calculations have become greatly simplified.

The current from a good sized gravity Daniell cell was passed through a resistance of 10000 ohms and the potential difference of 1/1000 of the cell's *E. M. F.* established at the terminals of the galvanometer, in whose circuit there was further inserted a resistance of 300 ohms. It was easy to so adjust the controlling magnet that when the feeble current thus produced was allowed to flow through the galvanometer the range of motion of the light-spot over the scale was some 70 or 80 divisions, so that a deflection of one scale division corresponded to 6 or 7×10^{-8} ampères. In the later experiments of the present series I used in place of the Daniell a calomel cell which was found to be very constant and whose *E. M. F.* I assumed in calculations to be $1 \pm 0{\cdot}01$ volt.

Three small mercury commutators arranged in a row were found to be very convenient for standardising and for resistance measurement. The mode of action can be easily seen from the accompanying figure. The wires *a a* served for throwing the experimental and leading wires, without moving them from their positions, into the fourth arm of the resistance box, and the wires *b b* for putting the galvanometer (of course much reduced in sensibility) into one of the diagonals of the box.



§ 31. The following table contains one of the experiments made on annealed soft iron wires 0·77 m.m. in diameter (from the same bundle as the wire of § 25). This is graphically represented in Fig. 1, Pl. IV.

Load in kilos.	*E. M. F. in micro-volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	+ 6.47	15	− 1.43
1	+ 6.61	14	− 2.07
2	+ 6.98	13	− 2.69
3	+ 6.72	12	− 3.43
4	+ 6.30	11	− 3.87
5	+ 5.19	10	− 4.50
6	+ 4.15	9	− 4.72
7	+ 2.74	8	− 4.86
8	+ 0.99	7	− 4.53
9	− 0.23	6	− 3.54
10	− 1.04	5	− 2.12
11	− 1.65	4	− 0.61
12	− 1.71	3	+ 1.37
13	− 1.89	2	+ 3.35
14	− 1.71	1	+ 4.91
15	− 1.23	0	+ 6.13
16	− 0.75		

§ 32. In most of my experiments, the present as well as those of the preceding paper, I have taken care to be as free as possible from the effect of magnetic disturbances on the galvanometer by working at night when shocks from work going on in the laboratory and other places in the neighbourhood had ceased. Since every arrangement in the thermo-electric circuit remained the same, the assurance may be had that, so far as relative magnitudes only are concerned, the results described in the preceding paper must be right.

§ 33. In the course of the present investigation, however, I have been gradually made aware of the inconstancy of the thermo-electric *E. M. F.* When one series of measurements was compared

with another carried out after even a few hours only, during which the wires had been cooled down to the atmospheric temperature, the latter series was usually found to be more to the negative side than the former in the scale of *E. M. F.*, and this to an extent which was indeed comparable with that of the total fluctuation of the thermo-electric *E. M. F.* Let us cite an example to make my meaning more concrete. The wires tested were cut from the same bundle as that of § 31. After being permanently elongated with a load of 16 kilos. the stretched wire was twice loaded up to the maximum load and unloaded down to zero. The observations then made are given in the following table :—

Load in kilos.	*E. M. F. in micro-volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	— 2.30	14	— 9.48
2	— 1.91	12	— 10.50
4	— 2.37	10	— 11.63
6	— 4.38	8	— 12.03
8	— 6.73	6	— 11.32
10	— 8.77	4	— 8.67
12	— 9.30	2	— 5.87
14	— 9.15	0	— 3.26
16	— 8.31		

The wires were then left undisturbed over night and on the next day heated for a while. After two successive loadings and unloadings (0—16—0 kilos.) the *E. M. F.* was measured, as in the following table :—

Load in kilos.	*E. M. F. in micro-volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	− 5.07	14	− 11.47
2	− 4.49	12	− 12.70
4	− 5.17	10	− 13.50
6	− 6.83	8	− 14.07
8	− 9.08	6	− 13.05
10	− 11.12	4	− 10.50
12	− 11.67	2	− 7.44
14	− 11.17	0	− 5.15
16	− 10.45		

Once more the wires were subjected to the same treatment, but for a shorter time (about 7 hours). The third series of observations is as follows :—

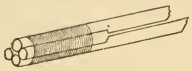
Load in kilos.	*E. M. F. in micro volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	− 5.90	14	− 12.68
2	− 5.61	12	− 13.63
4	− 6.19	10	− 14.78
6	− 7.88	8	− 15.20
8	− 10.16	6	− 14.04
10	− 12.31	4	− 11.31
12	− 12.72	2	− 8.59
14	− 12.26	0	− 6.03
16	− 11.60		

In Fig. 2, Pl. IV, the above are graphically expressed, the curves being numbered in the order of the foregoing tables.

Whence does this gradual shifting of the thermo-electric curve

as a whole arise ? That was the query which I set myself to solve, for if it is not due to some flaw in my experimental arrangements, or if it has root in the nature of the thing, then the labour of referring the *E. M. F.* to absolute measure would be to no good effect. It should be mentioned that I observed not merely a shifting towards the negative side, but sometimes also, though not often, a shifting towards the positive side.

The shifting would take place, as already described, after a number of hours, during which the wires had been allowed to cool to the atmospheric temperature and left undisturbed, or, as observed by me once, even after a number of alternate heatings and coolings. Could the standard cell have been really inconstant, the shifting might have been due to that, but that the cell's *E. M. F.* should change by 1/10 or more seemed to me to be exceedingly improbable. Therefore, in my efforts to account for the difficulty my attention was at first concentrated on the manner of making the junctions of the stretched and unstretched portions. As described in my preceding paper, I coupled them by putting their ends side by side and binding them together round and round with fine iron wires as firmly as possible. Lateral compressions thus introduced, one might suspect, could interfere with the production of the thermo-electric *E. M. F.* due to longitudinal tension. But seeing that the thermo-electric curves actually obtained, one series of measurements after another, are nearly parallel; that the points plotted on them are among themselves almost similarly placed ; and that the shifting is sometimes towards the positive side in the scale of *E. M. F.*, I cannot attribute such great and varying shifting to the interference of lateral compression. Wrong contacts at the junctions were another thing to be looked after. I cut short pieces from the experimental wires, laid them beside and along the junctions, and bound all the four pieces together as above described



(See the upper one of the annexed figures). The results obtained remained on the whole exactly the same as before. Still another mode of making the junctions was tried (See the lower of the annexed figures). A small cylinder of iron was divided unequally into two lengthwise, and in the larger segment a groove was cut for the wires to lodge in. The segments with the wires between them were firmly tied together by fine iron wire and then by hempen thread. I could not find anything that might be ascribed to this change in my arrangements.

Believing thus that the question as to the junctions may be set aside, I next sought for other causes. One thing which I think should be thoroughly examined is the iron-copper junctions (§ 4), for even when they are only very slightly different, (of course supposing them kept at the same temperature), an *E. M. F.* would yet be produced which could not be neglected in comparison with the one we have to measure. A series of observations was, therefore, made under the usual conditions, but with the junctions completely surrounded by powdered ice. Steam being then cut off and the wires allowed slowly to cool during the night, another series of observations was on the next day carried out, keeping the junctions in the usual condition. These series are represented in Fig. 3, Pl. IV, the curve *a* representing the former and the curve *b* the latter. Then, proceeding exactly in the same way but with less time intervening, I obtained another pair of curves *a'* and *b'*. Thin soft iron, 0·5 m.m. in diameter, was chosen for the experiments, because I thought it well not to lose much time in going through a cycle of loading and unloading and thereby allow the temperature of the iron-copper junc-

tions to vary so much as it might have done otherwise. Some regularities are discernible from the curves, but their interpretation seems not to be single. There may be an *E. M. F.* due to structural difference and this may vary at different temperatures ; or else, there may be an independent source of *E. M. F.* and this may vary not only at different temperatures, but also from time to time. Again, both these variations can quite possibly exist side by side. The wires being left undisturbed throughout the night and almost the whole of the next day, so that it could be assumed that all parts of my arrangements had attained the atmospheric temperature,[1] I closed the circuit of the experimental and leading wires through t e galvanometer and found a current which corresponded to an existence somewhere of an *E. M. F.* amounting to $-1{\cdot}7$ micro-volts. Closing the leading wires alone through the galvanometer an *E. M. F.* of nearly $-0{\cdot}1$ micro-volts was found to exist.

Where the seat of this *E. M. F.* is, and how it comes into existence, I can only guess at, and have no experimental data to base an answer on. At all events, it is certain that the *E. M. F.*'s measured and given in the table of § 31 are not pure inspite of the care which has been bestowed upon them, and cannot be referred to as such unconditionally.

Still another thing which cannot be overlooked with respect to the gradual shifting of the thermo-electric curve as a whole towards the negative side, is the magnetisation of the iron wires. From Prof. Ewing's experiments made on the relation, on the one hand, between the magnetic qualities of iron when under stresses and when not, and, on the other hand, the relations of the thermo-electric *E. M. F.* between them, and also from a few of my own experiments, I have

(1) The temperature of the cellar, where all of the experiments were carried out, was. 24.°5—25.°5.

been led to conclude that the problem of comparing the thermo-electric *E. M. F.* in different specimens of iron or in the same specimen under different conditions, is not to be attacked, even though all other questions have been cleared up, till I shall be in possession of a fuller knowledge of that relation, which, as I have convinced myself by experiments, has indeed a very intimate connection with my present subject of investigation.

§ 35. Steel was the subject of the next experiments, one of which is given in the following table. The wire was 0·5 m.m. in diameter and was tested after being well annealed.

Load in kilos.	*E. M. F. in micro-volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	− 2.01	12	+ 8.27
2	+ 0.21	10	+ 6.04
4	+ 2.01	8	+ 4.24
6	+ 3.50	6	+ 2.61
8	+ 5.28	4	+ 0.74
10	+ 6.68	2	− 0.95
12	+ 8.69	0	− 2.00
14	+ 10.17		

Examining the curve in Fig. 4, Pl. IV, in which the above numbers are graphically represented, we see that the effect of the thermo-electric hysteresis is here quite apparent, causing the "off" branch to deviate from the "on." After a few steps of loading, the initial gradient of the "on" branch becomes smaller, though very little, and under heavier loads the curve runs almost straight. As to the "off" branch the gradient becomes appreciably less and less as the unloading goes on, and at a somewhat quicker rate near the close of unloading. The "on" branch seems to show something like a point

of inflexion, though a very indistinct one, while the "off" is convex towards the axis of load; and in fact, the general form of the curve is such as may induce us to class it among those for hard iron.

Curves for steel hardened by drawing are almost identical with the above and as was the case with iron present nothing that calls for remarks.

By a series of experiments I have ascertained that from a smaller cyclic range of loading and unloading up to the greatest possible the form of the curve again remains exactly the same, and also that the effects of vibration are very small, and take place always in the same senses as in iron.

§ 36. Palladium comes next in the order of my experiments. My measurement completely confirms the remark of Dr. Cohn that it shows a large effect under comparatively low loads. Though I was fortunate enough to have in my possession a sample of it long enough for my arrangements, I could not multiply my measurements as in iron and steel. The wire was 0·4 m.m. in diameter and could be permanently elongated by a load of 1·5 kilos. The following experiment is one out of many, all of which were perfectly concordant with each other.

Load in kilos.	*E. M. F. in micro-volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	− 4.87	1.2	+ 4.26
0.4	− 1.83	0.8	+ 0.97
0.8	+ 0.97	0.4	− 1.95
1.2	+ 4.02	0	− 4.87
1.6	+ 6.56		

The graph of the experiment given in Fig. 5, Pl. IV, shows that the thermo-electric *E. M. F.* changes towards the positive side, varies

proportionally to the load applied, and does not present the least sign of hysteresis.

§ 37. Fourthly nickel. The specimen in hand was a rather poor one, yet inasmuch as experiments on another sample, alleged to be somewhat impure, showed the same general features, the following numbers may perhaps be taken as representing fairly well the thermo-electric effects of stress in nickel. Compare the curve in Fig. 6, Pl. IV.

Load in kilos.	*E. M. F. in micro-volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	− 2.51	7	+ 11.52
1	+ 0.90	6	+ 10.62
2	+ 4.63	5	+ 9.72
3	+ 6.44	4	+ 8.41
4	+ 8.59	3	+ 7.57
5	+ 9.44	2	+ 5.99
6	+ 10.51	1	+ 2.08
7	+ 11.30	0	− 2.48
8	+ 12.20		

Up to 5 kilos. the wire showed no sign of elongation, and at the load of 7·5 kilos. it drew very much. The "on" branch certainly deviates from the "off" and is on the negative side of the latter, their juxtaposition being thus opposite to that in iron and steel.

§ 38. In the fifth place, platinum. The specimen was 0·4 m.m. in diameter and could not be loaded with more than 1·5 kilos. Only after a number of loadings and unloadings did the thermo-electric *E. M. F.* become nearly cyclic and vary perfectly proportionally to the load applied. The result is given in the following table, with which the curve in Fig. 7, Pl. IV. is to be compared.

Load in kilos.	*E. M. F. in micro-volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	— 8.50	0.8	— 2.83
0.4	— 5.90	0.4	— 5.90
0.8	— 2.83	0	— 8.50
1.2	— 0.23		

§ 39. In the sixth place, silver. The specimen was not pure and being, further, very thin (0·26 m.m. in diameter) could not be loaded with more than 2·5 kilos. The thermo-electric *E. M. F.* was specially small and seemed to have been vitiated by extraneous *E. M. F.* The result of the measurements is given in the following table and graphically represented in Fig. 8, Pl. IV. The *E. M. F.* seems to decrease as the load is increased, a result contrary to that obtained by Prof. Ewing.

Load in kilos.	*E. M. F. in micro-volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	— 4.28	1.6	— 5.79
0.4	— 4.75	1.2	— 5.56
0.8	— 4.86	0.8	— 5.04
1.2	— 5.27	0.4	— 4.86
1.6	— 5.61	0	— 4.46
2.0	— 6.14		

§ 40. In the seventh place, copper. The specimen (0·8 m.m. in diameter) was commercical and was tested in hard drawn state. Here on account of being somewhat free from extraneous *E. M. F.* at the junctions, the readings taken, though small, were very regular

and smooth, as will be seen from the following table and Fig. 9, Pl. IV.

Load in kilos.	*E. M. F. in micro-volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	+ 0.36	12	+ 1.15
3	+ 0.53	9	+ 0.96
6	+ 0.78	6	+ 0.75
9	+ 0.92	3	+ 0.59
12	+ 1.13	0	+ 0.33
15	+ 1.33		

§ 41. In the eighth and last place, aluminium. I was induced to test this metal because its thermo-electric effect under tension was found by Prof. Ewing to be opposite to that of most of the other metals he examined, that is to say, he found that the *E. M. F.* decreases as the load is increased. The following table contains one of my measurements made on a specimen 1 m.m. in diameter and it confirms the above statement.

Load in kilos.	*E. M. F. in micro-volts.*	*Load in kilos.*	*E. M. F. in micro-volts.*
0	− 0.15	6	− 0.45
2	− 0.25	4	− 0.36
4	− 0.31	2	− 0.19
6	− 0.49	0	− 0.10
8	− 0.55		

§ 42. To resume, I repeat here Prof. Ewing's remark that "So far there is no evidence that the peculiar behaviour of iron,....., is

not peculiar to that metal." In fact, that which makes iron (and also steel) magnetically remarkable and thermo-electrically singular, seems to have its ground in the characteristic molecular constitution of that metal. In other metals examined, the thermo-electric hysteresis with respect to longitudinal tension is either very insignificant or entirely absent. In them, excepting nickel, changes of *E. M. F.* are nearly proportional (either increasingly or decreasingly) to the loads applied.

Notes on the Topaz from Mino,

By

Tadasu Hiki, *Rigakushi.*

College of Science, Imperial University.

With Pl. V.

Occurrence.—In the northern part of the district Ena-gōri, Province Mino (Central Japan), there is an outlier of a great granitic *massif* of the Kiso range. The well-known Kiso river, which drains this range, comes from the province of Shinano, and flows through western Mino with broad alluvial plains on both sides. In the eastern portion of the district, that is, on the northern side of the river, stream tin is worked at present within the area of about four square kilometers. Many tributaries of the Kiso join here with the main stream, among them the Tengawa, the Chibaragawa and the Kizumizawagawa are worth mentioning. The latter two are rich in topaz and other minerals. Naegi, Takayama, Hirugawa, and Ichinose are also tolerably well-known for the occurrence of topaz in this tin-field.

Most of the crystals of topaz, which will be here described, are from these localities. The district in question is hilly and the whole mass of granitic elevations is surrounded by quartz-porphyry. Loose topaz may be easily collected from the surface soil in the regions of granite and quartz-porphyry; or from the plusiatic deposit, exclusively derived from these rocks. Besides, they are also found in small rivulets and marshes, and in cultivated soil, associated with cassiterite. The faces of the crystals are roughened by friction and their edges

rounded, especially in large specimens ; but small crystals with sharp edges are met with not infrequently. The crystals are well defined in those rare cases in which they occur in veins of smoky quartz forming a network in disaggregated granite. Granite seems to have been the mother rock of the topaz and of the minerals found with it in diluvium, viz., cassiterite, magnetic iron sand, smoky quartz, tourmaline, beryl, muscovite, biotite, orthoclase, plagioclase, sapphire, gold, pyrites, fluorite, wolframite, fergusonite (?), &c., for these minerals are apparently all to be found in quartz veins in the granite.

Literature.—Crystals of topaz from the provinces of Mino and Ōmi,[1] were first studied by T. Wada.[2] He mentioned, that they bear some resemblance to those from the Urals and Schneckenstein. The late Assistant-Professor Y. Kikuchi[3] has given a brief account of topaz from Mino, and classified it under three types. A. Hahn[4] has described above two hundred specimens from Mino. W. D. Matthew[5] has also described seventy-five crystals from Ōmi and twenty-five from Mino. Lastly, Penfield and Minor,[6] have written about the chemical and physical characters of the topaz from Mino.

Y. Kikuchi left his investigation unfinished ; and his collection and mine, (the number of crystals examined being above five hundred) form the subject of the present paper.

Character of the Crystals.—The crystals are short columnar forms, and vary considerably in dimensions, the width from 0.5 to 10 c. m., and the length from 1.5 to 30 c. m. They are distinctly hemimorphic, when both ends are developed. Parallel growth of two individuals, is sometimes observed. Most of the crystals are transparent;

1. Another topaz locality of Japan.
2. Sitzungsberichte der Gesellschaft Naturwissenschaftlicher Freunde zur Berlin. 1884.
3. Rigaku-kyokai-Zasshi. 1887.
4. Groth, Zeitschr. f. Kryst. u. Min. 1893.
5. Neues Jahrbuch. f. Min. &c. Referate. 1894.
6. Groth, Zeitschr. f. Kryst. u. Min. 1894

and are sometimes coloured different tints of green and pink, which disappear on long exposure to sun light. Pleochroism in large specimens can be observed without an instrument. The following axial colours vary in intensity, according to the pellucidity :

$\mathfrak{a}$ = sky-blue.
$\mathfrak{b}$ = pink.
$\mathfrak{c}$ = yellow.
The absorption is $\mathfrak{a} > \mathfrak{b} \geqslant \mathfrak{c}$

Some of the larger specimens are coloured differently along their horizontal axes. Nothing is to be specially mentioned, with respect to the optical characters of this topaz, of which the following optical constants have been measured.

	α	β	γ	2V	2E
For yellow.[1]	1.6134	1.6178	1.6233	62°52′	115°3′
For red.[2]	1.6113	1.6142	1.6162	62°24′	113°33′

Enclosures are common; they are cassiterite, tourmaline, chloritic substance, as well as liquids containing bubbles. The specific gravity is 3.556–3.566 ; mean 3.561. This is nearly the same as that of crystals from the Urals and from Brazil.

Crystal Faces.—The faces, which I have recognised are as follows :

Brachydomes.	$f = (021)\ 2\,P\,\breve{\infty}$	$y = (041)\ 4\,P\,\breve{\infty}$
	$X = (043)\ \frac{4}{3}\,P\,\breve{\infty}$	
Macrodomes	$d = (201)\ 2\,P\,\breve{\infty}$	$h = (203)\ \frac{2}{3}\,P\,\bar{\infty}$
Pyramids.	$u = (111)\ P$	$o = (221)\ 2\,P$
	$i = (223)\ \frac{2}{3}\,P$	$v = (121)\ 2\,P\,\breve{2}$
	$r\dagger = (241)\ 4\,P\,\breve{2}$	$x\dagger = (243)\ \frac{4}{3}\,P\,\breve{2}$

1. Using sodium carbonate.
2. Using strontium chloride.
† These are faces now first observed in Japanese crystals.

Prisms.	$M = (110)\ \infty P$	$l = (120)\ \infty P \breve{2}$
	$m = (230)\ \infty P \breve{\frac{3}{2}}$	$g = (130)\ \infty P \breve{3}$
	$\pi = (250)\ \infty P \breve{\frac{5}{2}}$	$O = (560)\ \infty P \breve{\frac{6}{5}}$
	$\lambda = (470)\ \infty P \breve{\frac{7}{4}}$	$T = (350)\ \infty P \breve{\frac{5}{3}}$
Base.	$c = (001)\ 0 P$	
Brachypinacoid.	$b = (010)\ \infty P \breve{\infty}$	

List of the Facial Angles of Topaz.

	Mino. Measured by the Author.	Ural.[1] Kokscharov.		Japan.[2] Hahn.	South[3] Africa. Hintze.
		Calculated.	Measured.	Measured.	Measured.
M : M=(110) : $(1\bar{1}0)$	55° 42′ 0″	55° 43′ 0″	55° 43′ 0″	55°45′–55°44′	55° 43′ 0″
M : m=(110) : (230)	10 31 24	10 32 58	10 32 30	10 32 0	10 33 0
M : l=(110) : (120)	18 44 0	18 43 52	18 43 45	18 43 0	18 42 0
l : g=(120) : (130)	11 10 20	11 10 20			11 8 30
l : m=(120) : (230)	8 6 0	8 10 54	8 2 0		
g : b=(130) : (101)	32 15 30	32 14 18			32 15 0
l : l=(120) : $(1\bar{2}0)$	86 48 0	86 49 16	86 48 0	86 21 0	
M : o=(110) : (221)	26 5 30	26 5 52	26 7 0		26 7 0
l : o=(120) : (221)	31 49 0	31 44 8			
o : o=(221) : $(2\bar{2}1)$	49 34 30	49 37 28	49 37 9	49 39 0	
f : o=(021) : (221)	52 33 0	52 33 28			
d : o=(201) : (221)	24 46 30	24 48 44	24 48 30	24 50 0	24 48 30
u : o=(111) : (221)	18 17 30	18 18 53	18 19 0	18 17 0	18 17 30
y : o=(041) : (221)	54 45 0	54 50 14			
u : u=(111) : $(1\bar{1}1)$	38 59 0	38 59 54	38 59 0		
d : u=(201) : (111)	26 53 30	26 55 42	26 55 40		26 55 0
i : u=(223) : (111)	11 23 22	11 21 10			11 21 30
f : u=(021) : (111)	42 32 0	42 32 48	42 32 17		
M : u=(110) : (111)	44 15 30	44 24 45	44 24 50		44 25 0
l : u=(120) : (111)	47 21 30	47 25 47			

i :	$i=(223)$: $(\bar{2}23)$	30° 27′ 30″	30° 29′ 0″	30° 28′ 0″		
c :	$i=(001)$: (223)	34 12 0	34 14 5	34 13 0		34° 12′ 0″
M :	$d=(110)$: (201)	39 20 0	39 20 43	39 20 30		39 19 0
c :	$d=(001)$: (201)	61 1 30	61 0 40	67 1 0		61 0 0
c :	$f=(001)$: (021)	46 18 30	46 21 0			43 38 0
y :	$f=(041)$: (021)	18 40 30	18 41 22			18 40 0
c :	$h=(001)$: (203)	31 2 0	31 1 56			
c :	$X=(001)$: (043)	32 29 30	32 27 19			
r :	$o=(241)$: (221)	17 54 0	17 56 45			
v :	$o=(121)$: (221)	19 23 30	19 24 50			
v :	$f=(121)$: (021)	33 8 0	33 8 40			
M :	$\pi=(110)$: (250)	24 55 0				25 1 0
M :	$O=(110)$: (560)	4 32 0				
M :	$\lambda=(110)$: (470)	14 52 0				15 17 0
M :	$T=(110)$: (350)	13 28 0				13 30 0
f :	$f'=(021)$: $(0\bar{2}1)$	87 7 0				

The axial ratio is

$$\breve{a} : \bar{b} : \dot{c} = 0.528356 : 1 : 0.475587.$$

Of the six different kinds of pyramids, u, o, i, v, r, and x, the first two occur most frequently, u being generally larger than o. The faces r, v, and x are never found in large crystals; they have, however, been observed in ten out of three hundred smaller specimens. The pyramids appear more etched than the other faces.

Among macrodomes, d is the commonest, and h is only occasionally observed.

Among brachydomes, f is generally present, and in many cases well developed. The face y is less frequent; and occurs only in

1. Kokscharov; Materielien zur Mineralogie Russlands.
2. *loc. cit.*
3. Groth, Zeitschr. f. Kryst. u. Min. 1889.

those crystals, in which pyramids as well as base are prominent. The face X, which is very common in the Ōmi crystals (see fig. 20), has been observed only in two specimens from Mino. The etched figures on f and y appear in some cases like pyramids.

Prismatic faces are much striated. The commonest are M and l, while m and g occur less frequently. The other faces (O, π, λ and T) are scarcely recognisable. Besides, however, $\infty P \frac{\breve{21}}{20}$ and $\infty P \frac{\breve{11}}{4}$ have been noticed, by Hahn and by Matthew respectively.

The basal-pinacoid is found quite frequently on small crystals, in which it is distinguished from cleavage, by its natural etched figures. In large individuals, the base is seldom observed.

The brachy-pinacoid is frequent; while the macro-pinacoid, though mentioned by Matthew as in Japanese crystals, has not yet been observed in our collection.

Different Types of Crystals.—Y. Kikuchi has subdivided the crystals of topaz from Mino into

(I) Domal type.
(II) Pyramidal type.
(III) Base-pyramidal type.

To these, I wish to add one more, the Tabular type (IV). The four types are, however, connected by intermediate forms.

Type I. Domal type. (fig. 1–fig. 3).

Crystals more than 0.5 c. m. in width are mostly simple and generally belong to this type. Smaller crystals, however, are richer in faces, and rarely belong to this type. In this type f, M, and l are predominant, while the pyramids u and o are subordinate. The face o is less common than u. The macro-dome d is often observed, but is generally small. The brachydomes X and y are rare.

Type II. Pyramidal type. (fig. 4–fig. 10).

The prevailing faces in this type are *o* and *i*, accompanied by *r* in rare cases. The brachydome *f* is always present, *y* occurs frequently and the brachypinacoid *b* is rare. The prisms, *M*, *l*, and *m* are pretty often found, while many other prisms are difficult to distinguish.

Type III. Base-pyramidal type. (fig. 11–fig. 18).

Crystals of this type show the most complex combinations, and are rather common in smaller individuals. The pyramids *u*, *o*, *i*, *r*, *v*, and *x*, belonging to the vertical zones of the prisms *M* and *l*, are all here represented. The brachydomes *y*, *f*, and *X* are developed nearly of equal size. All the prismatic faces occur in this type.

Type. IV. Tabular type. (fig. 19).

The peculiarly flattened form is due to suppression of two parallel faces in one of the prisms *M* and *l*. Such an alteration in the development of faces has not yet been noticed in crystals from the Urals, Schneckenstein, and South Africa. These crystals are, however, in general aspect, very like the different types of our specimens.

Etched Figures.—Natural etched figures are comparatively frequent in our specimens, but it is difficult to find out their crystallographic significance.

On *c*. (E. 1.) There is observed a group of small rectangular pyramids, with their bases extending in the direction of the macro-axis. The figures seem to have been produced just in the same way, as in the Ōmi topaz, where we find on the same face long rectangular impressions (fig. 20. *b*.) parallel to the macro-axis. In a further stage of corrosion they appear in the shape of grooves leaving between them high rectangular pyramids, as represented in fig. 20. *a*. The figures observed by Laspeyres[1] and Pelikan[2] have not been found.

1. Groth, Zeitschr. f. Kryst. u. Min. 1877.
2. Tschermak, Min. u. Petro. Mitth. 1890.

On *f*. (E. 2.) Small eminences in the shape of isosceles triangles, with curved sides and a pretty acute apex, are produced. Their base is parallel to the edge *c* : *f*, while their other two sides are parallel to the edge *l* : *f*. Besides, there are observed irregular, ring-shaped markings resembling cracks. The etched figures seen by Pelikan have not been noticed.

On *u*. (E. 3.) The etched figure consists of fine parallel striæ and some irregular lines across them.

On *o*. (E. 4.) Two different kinds of etched figures; namely, triangular eminences and rectangular depressions are here produced. The triangular figures are very like those described by Pelikan ; but possess rather curved sides. The same figures are again found in the topaz from Ōmi. The triangles are equilateral and one of the sides is parallel to the edge *o* : *M*.

On *M*. (E. 5.) The etched figure observed by Pelikan on this face has not been noticed in our topaz. There are, however, long rectangular eminences parallel to the edge *M* : *M*. Besides we find peculiar impressions, whose curved sides face in opposite directions upon the two adjacent faces of *M*.

On *l*. (E. 6.) Small narrow impressions, bounded by straight and curved sides, which seem to be essentially the same as the trapezoidal figures observed by Pelikan.

On *d*. (E. 7.) Numerous irregular etched figures are found.

Mercury Perchlorates.

By

Masumi Chikashige, *Rigakushi.*

College of Science, Imperial University.

Having, at the suggestion of Dr. Divers, prepared mercuric and mercurous perchlorates, with the object of examining their behaviour when heated, I have found their properties to be not quite as described by Serullas in 1830, and by Roscoe in 1862. The earlier memoir, which appeared in *Ann. Chim. Phys.*, [2], **45**, 270, I have not seen, and make my statements about its contents on the authority of the larger works on Chemistry. Sir Henry Roscoe's well-known paper on Perchloric acid is to be found in full in *Proc. Roy. Soc.*, **11**, 502, and also in *Liebig's Annalen*, **121**, 346.

Most of the hydrated perchloric acid, I have used in my experiments, was prepared from potassium chlorate and hydrofluosilicic acid, following Roscoe, but some of it by the slight modification of this process, more convenient at the present time, consisting in replacing the above salt and acid by barium chlorate and sulphuric acid. It is a fact not altogether unknown, though not mentioned by Roscoe, that the hydrated acid is slightly decomposed when it is distilled, and becomes contaminated with a little chlorine and hydrochloric acid in consequence. I find that heating the distilled acid for a short time in the air is sufficient to free it from these impurities.

Mercuric perchlorate.

Mercuric perchlorate is obtained when mercuric oxide is triturated with aqueous perchloric acid until the resulting solution begins to grow turbid from the presence of basic salt. The solution is filtered, preferably through asbestus, mixed with a few drops of perchloric acid, and evaporated at a gentle heat to a small volume. Evaporation is then continued at the common temperature, over sulphuric acid, until the salt crystallises out. If necessary, it may be recrystallised after dissolving it in a very little water. It is quite stable, but needs some care to dry it, for in a desiccator it slowly effloresces, and in the air it very quickly deliquesces (Serullas), while by slight rise of temperature it melts. Preserved for a day or two in bottles, however, its upper layers become dry by draining, and may then be quickly pressed between folds of paper.

Mercuric perchlorate crystallises in slender rectangular prisms, as described by Serullas. Being exceedingly soluble in water, as well as very hygroscopic, its slender crystals rapidly liquefy when exposed to the air. It reddens litmus (Serullas), but its freedom from acid can be shown by adding excess of sodium chloride to its solution, which renders it neutral.

It shows a slight tendency to decompose with water. In absence of any excess of acid, its solution deposits basic salt during evaporation by heat. Also, its slow efflorescence in the desiccator is the result of loss of acid as well as of water; so that the effloresced salt leaves some insoluble basic salt when dissolved in water.

Alcohol decomposes it more freely. The effect of this agent has been described by Serullas, but I will here give a more definite statement of its action, as observed by myself, than I find given in the handbooks. Alcohol at once decomposes the crystals of the salt, leaving

undissolved a white basic salt. This, again, is decomposed by water, which leaves behind impure mercuric oxide. Alcohol added to an aqueous solution of mercuric perchlorate gives an orange precipitate, mainly mercuric oxide. As to the formation of mercurous oxide or mercurous salt, which is mentioned as taking place on evaporating the mother-liquor, that happens to a small extent only, and because mercuric salts are reduced by hot alcohol.

Of the composition of mercuric perchlorate all that is known is that, on the authority of Serullas, it is expressed by $Hg(ClO_4)_2$; it passes for an anhydrous salt (Roscoe and Schorlemmer's *Treatise;* Muir and Morley's *Watts' Dictionary*, etc.). It proves, however, to be a hydrated salt, with as much as six mols. of water, which, though it can be readily got from the salt by heat, cannot well be directly estimated, since perchloric acid is liberated along with it from the first. The composition of the salt was determined by precipitating the mercury as sulphide and obtaining the perchloric acid from the filtrate as its potassium salt, with the precautions given in Roscoe's paper. The formation of a very little sulphuric acid in removing the excess of hydrogen sulphide cannot be avoided, and this comes out in the potassium perchlorate and, small as it is, has to be taken account of. In the second of the analyses, the results of which are here given, the mercury was precipitated by gaseous hydrogen sulphide without addition of acid; in the first, it was precipitated by adding at once excess of hydrogen-sulphide-water, and then a cubic centimeter of dilute sulphuric acid to coagulate the mercury sulphide. The total sulphuric acid having been determined, the corresponding quantity of potassium sulphate was deducted from that of the potassium perchlorate and sulphate together. In consequence of what has just been stated, this procedure introduced no complication, while the use of hydrochloric acid was precluded, as interfering with the determination of

the perchloric acid. The calculation is for $Hg(ClO_4)_2,6H_2O$.

	Calc.	I.	II.
Mercury	39·47	39·26	38·95
Perchlorate radical	39·25	38·90	38·82
Water	21·30		

Behaviour of mercuric perchlorate when heated.—Mercuric perchlorate, as dry as possible, melts at about 34°, in dry air. Heated in a long narrow tube, closed only at its lower end, the salt melts to a colourless liquid, which boils freely, without noticeable change, even in a bath of boiling sulphur. In reality, it is decomposed, and at temperatures far below this, but since the products of its decomposition, which boil off, condense and flow down again, the salt is recovered when the tube is cooled.

Even at the common temperature, as already mentioned, mercuric perchlorate very slowly decomposes in dry air, but, in a current of dried air at 120°, the evolution of water and perchloric acid becomes manifest in the shape of white fumes. By raising the temperature gradually and maintaining it then at 150° until the weight of the residue becomes constant, there is obtained a homogeneous and apparently definite compound.

Oxymercuric perchlorate, this compound, is white and amorphous; it is unchanged by the heat of boiling mercury, and only slowly affected by that of boiling sulphur. Heated to a point a little below that at which mercuric oxide freely decomposes, it is completely changed into oxygen and chlorine gases, sublimates of mercuric and mercurous chlorides, and a residue of mercuric oxide. By water it is decomposed into mercuric perchlorate and mercuric oxide, besides insignificant quantities only of chloride and chlorate. In a quantitative experiment, it was found to yield to water, mercury 12·64, and perchlorate radical 12·90 per cent. of the weight of the salt which had

been heated to form it. Therefore, water dissolves out normal mercuric perchlorate, and, since 12·90 is almost exactly the third part of 39·25, the percentage amount of perchlorate radical in the original salt, the change effected by heat may be formulated thus:—

$$3[Hg(ClO_4)_2,6H_2O]=O_2Hg_3(ClO_4)_2+4HClO_4+16H_2O;$$

$O_2Hg_3(ClO_4)_2$ expressing the composition of the oxymercuric perchlorate.

Mercurous perchlorate.

Mercurous perchlorate can be very quickly prepared by violently shaking a solution of mercuric perchlorate with mercury for a few minutes, after which nothing but the mercurous salt will be found in the solution. Such a solution cannot be left for days, or be heated long on a water-bath, without letting fall some basic salt, but a concentrated solution can be evaporated in a vacuum-desiccator fast enough to avoid this. With rapid evaporation, the salt is obtained in fine needles, as described by Serullas. These needles are flat and, with slower evaporation, develope into flattened prisms or plates of considerable size.

The salt is exceedingly soluble in water, by which, in large quantity, it is often decomposed. It causes a sensible fall in temperature in dissolving. Its solution is neutral to litmus. Serullas found the salt to be unchanged by exposure to air, and must, therefore, have been working in very dry weather. For it is, as Roscoe describes it, very deliquescent, though less so than the mercuric salt. According to this chemist, it does not lose water, either at 100° or *in vacuo* over sulphuric acid. This is not really the case, but the loss of weight is slow enough in either case to be easily overlooked. In about two weeks in a vacuum-desiccator, the loss reaches nearly six

per cent. and then ceases. This loss, though mainly that of water, includes also that of a little acid. A loss of half its water would amount to 5·36 per cent. of its weight. At 100°, in a current of dry air, it loses about 2 per cent. of water in six hours, a mere trace of acid also escaping, as was proved by placing litmus-paper in the issuing current of air. In another six hours it loses about 2 per cent. more in weight, including now a notable amount of acid.

As already stated, the salt is gradually decomposed by water. The white basic salt thus produced becomes, when washed with water, black from loss of acid. Alcohol decomposes the solid salt into soluble acid-salt and white basic-salt, which is also blackened by washing with water, but not by alcohol. Alcohol, added to an aqueous solution of the salt, has no immediate effect.

In analysing the salt, the perchloric acid was determined in the same way as in the mercuric salt, after removal of the mercury as sulphide. The mercury was estimated in a separate portion of the salt by precipitation as mercurous chloride. The composition of the salt has been given by Roscoe as that expressed by the formula, $(HgClO_4)_2,6H_2O$, he having found the mercury to be 56·60 per cent., in perfect agreement with the calculation for that formula. Nevertheless I have assured myself, by examining different preparations, that the crystals I can obtain hold always, when not visibly moist, only four mols. water—$(HgClO_4)_2,4H_2O$.

	Calc.	I.	II.	III.	IV.
Mercury	59·61	59·00	58·90	—	—
Perchlorate radical	29·66	—	—	29·60	29·50
Water	10·73	—	—	—	—

It might seem from our respective results, that we had examined different hydrates, but in the several preparations I made of the salt, I never met with but one form of crystal which, with rapid evaporation

in the vacuum-desiccator, was that of fine needles, as described by Serullas, and as got by Roscoe presumably, for he makes no mention at all of the form of his crystals. By somewhat slower evaporation in the desiccator, much larger crystals were obtained, and found preferable for analysis, as being more easily freed from mother-liquor. But I took care to use the fine needles in my analyses, as well as the plates. One of the three samples analysed, marked above, II, III, IV, I cannot say now which, was of fine needles that had formed the first crop, while the other two were of larger crystals that had been the second crop from the same preparation. Sample I was of another preparation. If Roscoe's preparation was a higher hydrate than that I have obtained, it should not have shown itself able, even for a short time, to bear the heat of 100° or the dry air of a desiccator without loss, as he found it to do.

Behaviour of mercurous perchlorate when heated.—Mercurous perchlorate, unlike the mercuric salt, has no melting point. Quickly raised to about 190°, the salt becomes partly liquid for a short time, but only from the presence of unvolatilised acid along with basic salt. When gradually heated, the salt does not show even this false fusion. At 100°, the crystals of the salt decrepitate. At this temperature, it loses acid only very slowly, so as to be still all soluble in a little water after two or three hours heating in an open tube. At about 150°, its crystals slowly intumesce and become opaque. Not only basic salt is then formed, but also a little mercuric salt and a trace of chloride. At 170°, for some hours its decomposition goes farther: more mercuric salt is formed and a good quantity of chloride, as well as some chlorate (detected by decomposing with zinc and sulphuric acid). At 200°, white fumes escape, containing mercuric chloride. The more the salt is heated, the more basic it becomes, the redder and the larger is the residue left by water, and the less mercurous nitrate this residue yields

when dissolved in nitric acid. Heated to 357°, it suffers no further change, but, at 444°, decomposes slowly. The products are then the same as those of heating the residue from the mercuric salt, but only very little free chlorine can be detected. No metallic mercury appears among the products.

Potassium nitrososulphate.

By

Edward Divers, M.D., F.R.S., Prof.,

and

Tamemasa Haga, F.C.S. *Rigakuhakushi,* **Asst. Prof.**

Imperial University.

Hantzsch has recently expressed the opinion (*Berichte*, **27**, 3264), that there exist two potassium nitroxysulphites, one being Pelouze's nitrosulphate (the nitrososulphate of Henry Watts and of ourselves), the other a salt obtained by Raschig (*Annalen*, **241**, 230) and again by himself. This opinion we cannot share for reasons we proceed to state.

Above all, Hantzsch is mistaken in holding that Pelouze found the nitrososulphates to be precipitable by barium salts. The latter expressly states the contrary, in proof that these salts cannot be taken to be sulphates, with nitrous oxide acting merely as water of crystallisation. There is, indeed, a sentence in his paper calculated to mislead on this point, wherein he says that the solution of the 'new salt' gives a precipitate with a barium salt, which, when washed, is soluble in nitric acid. For this precipitate, as the context enables one to make out, is only that caused by impurities, such as carbonate, in the potassium hydroxide employed in the experiment then described, which precipitate he desired to show to be free from sulphate, by its solubility in acid. Thus, if our reading of Pelouze be correct, and it

actually is the reading of other chemists before us, that property, which Hantzsch regards as, above all, characteristic of Pelouze's salts, has no existence in fact.

Hantzsch says, further, that the greater decomposability of his own potassium salt stands in striking contrast with the relatively great stability of Pelouze's salt, which, according to the latter, can be purified by dissolving it in boiling water and then recrystallising, with loss only of a small part of it through decomposition. The greater instability of Hantzsch's preparation is seen, according to him, in the fact that its solution in water decomposes somewhat quickly even at the common temperature, and with effervescence when gently heated.

But we find both descriptions to be true of one and the same preparation. Any sample of the salt, as obtained by us in a strongly alkaline mother-liquor, following Pelouze's directions, which has been thoroughly well drained on a tile, so as to be almost pure and, though alkaline to litmus, yet without the least caustic taste, can be purified, as Pelouze says, by dissolution in the proper quantity of boiling water and quick cooling of the solution. There will, it is true, be brisk effervescence, but the greater part of the salt will be recovered and will be free from sulphate, after draining on a tile. Then, again, the pure salt can be dissolved in just sufficient boiling water, with but little effervescence and quite small loss, if only to the water has been added a few drops of dilute solution of potassium hydroxide, and that the hot solution is cooled quickly by immersion in cold water. The same crystals may then be redissolved in their mother-liquor, and the solution brought to full ebullition over a naked flame, and, yet, much of the salt be recovered, provided the solution is quickly cooled. Further, using each time water at 50° with no alkali at all, the pure salt may be dissolved and recrystallised four times over, collecting and draining the crystals each time, and testing them for purity, though there is

here, such great loss, from one cause and another, that from ten grams the quantity of pure salt recovered the fourth time amounts to only a fraction of one gram. Now, such a salt as this, fully coming up, as it does, to every expectation based on Pelouze's description, will quite freely effervesce in its solution at 60° or above, and will all decompose in a day or two, even at common temperatures, thus behaving in accordance with Hantzsch's description. Pelouze, we may add, found the less stable ammonium nitrososulphate to decompose slowly in solution even at 0°, and quickly with effervescence at 40°.

Another point of contrast noticed by Hantzsch in the effect of heat on the two salts is that, while the salt he can prepare is gradually but fully decomposed when heated up to about 90°, into sulphate and nitrous oxide, Pelouze states that he found his salt not to lose weight and not to decompose at 110°–115°.

We find the salt prepared by us to behave conformably with Hantzsch's account, and feel ourselves justified in setting down Pelouze's contrary statement to some oversight on his part, not ourselves meeting in his description of his salts with that exactness, which Hantzsch speaks of. Our own observations amount to what follows. At the bottom of a test-tube, immersed in oil, the pure salt, on two occasions, exploded at 91°, when heated in well-dried air. In a capsule in the ordinary air-bath, some of the same pure salt reached 108° before it exploded. Again, at the bottom of a test-tube in oil, in a gentle current of well-dried hydrogen, the salt exploded also at 108°. The decomposition is an exothermic one, and we are disposed to attribute this difference from the tube experiments in air to the well-known great cooling effect of the hydrogen being about equal in the test-tube to that of the use of an open vessel in a capacious air-bath, rather than to the exclusion of air by the hydrogen. In another experiment made in dried hydrogen, the salt lost only 10 %, that is,

half the total loss of weight, in $2\frac{1}{4}$ hours, at 95°, and the whole, or 20 %, not before the salt had been heated twelve hours. Thus, the loss in weight is slow, and a heat, mistaken for 110° (107°), maintained for only a few minutes, would have had so small an effect as perhaps, to have deceived Pelouze. When the salt does suddenly decompose, a marked rise of temperature accompanies the change, and this may have caused him to name 130° as the decomposition point. If these suggestions are rejected, as to how Pelouze's statements may be explained away, we have still in this difference in behaviour to heat, the only one unaccounted for between Hantzsch's and Pelouze's preparations.

From Pelouze's account it is to be inferred that, while in presence of moisture and acids, potassium nitrososulphate decomposes into potassium sulphate and nitrous oxide, it is converted by dry heat wholly into sulphite and nitric oxide. Hantzsch has found, however, that by dry heat not more than 20–26 % of the salt is changed into sulphite and nitric oxide, the rest becoming sulphate and nitrous oxide. But there is nothing to show that Pelouze worked quantitatively in the matter. Besides, Hantzsch himself has found that silver-potassium nitrososulphate does wholly decompose into sulphite * and nitric oxide by heat, thus greatly lessening the weight that might be attached to this supposed difference.

Heating the salt in dried hydrogen until it exploded at 108° we got results showing that 28.2 in one case, and 29 parts per 100 in another case, had been changed into sulphite. Our mode of working,

* Impressed by the stability of silver-potassium sulphite, Hantzsch is led to recognise in it that constitution which one of us and Shimidzu, unknown no doubt to him, had long since given it (*J. Chem. Soc.* 49, 581). Further, that it is like the mercury sulphites, which according to Barth, he says are sulphonates. We not only agree with this view of the constitution of these salts, but would point out that Barth in the paper quoted by Hantzsch, fully credits Divers and Shimidzu with that view, and then adopts it and confirms it.

however, was not only a little different from that adopted by Hantzsch, but we had to estimate the nature of the change in another way. He exploded the salt and noted its loss in weight, and from this calculated how much of it had given off nitric oxide, and how much nitrous oxide. We could not do this, since much of the residue was always blown out of our tube. Instead, therefore, we determined by the iodine method the amount of sulphite in a weighed quantity of the residue. There was always a trace of nitrite to be found.

We have now noticed all the points of supposed difference between Pelouze's nitrososulphate and what Hantzsch has designated the Raschig salt, and have said enough, we believe, in the light of our own experiments, to make it reasonably certain that the two salts are one. We will now turn to Raschig's other salt.

This salt, which Raschig and Hantzsch have erroneously taken to be identical with Pelouze's potassium nitrososulphate, has two specific characters :—it gives a barium salt insoluble in water, and it yields dipotassium oximidosulphonate when its solution in weak potash is made to crystallise, either by cooling or by evaporation. It may be mentioned here, parenthetically, that we have found it impossible to get any oximidosulphonate from pure potassium nitrososulphate. To get this salt of his, Raschig had to evaporate over sulphuric acid until crystalline crusts formed, the solution produced by passing nitric oxide through potassium sulphite. Other workers have always got their product crystallising out during the absorption of the gas.

Hantzsch has tried in vain by various means, to prepare this salt. As for ourselves, in whatever way we have worked, we have always got Pelouze's nitrososulphate and no other along with it, though we have used a freezing mixture of ice and salt, the cold of melting ice, or the prevailing temperature, have had much potassium

hydroxide present or none at all, have worked for abundant yields of salt from the first, or have stopped before crystals had begun to form and then evaporated the solution over sulphuric acid, or, lastly, have evaporated the mother-liquors of the first formed crystals.

Potassium nitrososulphate, we may here state, is soluble in a little more than 8 parts of water at 14½°, according to our own determination, but is less soluble in presence of potassium hydroxide. It can readily be recovered by evaporating its solution over sulphuric acid, though not without loss in the absence of alkali.

In composition, so far as potassium and sulphur are concerned, which alone were estimated by Raschig, this nitroxysulphite of his agrees very nearly with his 'basic potassium dihydroxylamine sulphonate' (*op. cit*, p. 192) in a state of dampness. From that salt, too, it appears to be indistinguishable by any properties, save an inconstant one. Raschig says that, on several occasions, this nitroxysulphite was observed to develope some nitrous oxide in being dissolved in hot weak potash solution. But so would Pelouze's salt have done, with which, therefore, it may have been occasionally mixed, in the crystalline crusts of an evaporated solution. Otherwise, both the dihydroxylamine salt and this nitroxysulphite, even in dilute solution, give a barium precipitate soluble in acids, the solution quickly depositing barium sulphate. Both salts, it must be inferred, freely evolve nitrous oxide when acidified, and both are decomposed by water and then yield oximidosulphonate.

Reserving for future publication all details, we may state now that oximidosulphonates and also salts similar to, if not identical with, the obscurely known dihydroxylamine salt, are obtainable very easily from potassium sulphite and nitrous fumes. Even with nitric oxide, unless quite special precautions are taken, at least minute quantities of dipotassium oximidosulphonate are always formed, and can be

separated with care, by evaporating the mother-liquors of potassium nitrososulphate almost to dryness, with sometimes the addition of alcohol; while without precautions to keep the nitric oxide colourless and all air absent, this salt forms quickly in notable quantity. Now, did Raschig take these precautions? Presumably he did, but there is not a word in his memoir to show that he was conscious of this liability to err, or that he took any such precautions as, for instance, were taken by Hantzsch, to have his nitric oxide pure. Until something more definite can be stated of the way to form such an isomer of Pelouze's potassium nitrososulphate as Raschig has described, its existence remains unproved; for his preparation, for aught he has shown, could have been Pelouze's salt mixed with some such salt as his own potassium dihydroxylamine-sulphonate.

In a short paper, published some years ago (*J. Chem. Soc.*, **47**, 364) we made known the fact that, although the alkali nitrososulphates had appeared, hitherto, to be incapable of bearing ordinary double decomposition with other salts, we had yet found them capable of a few such changes, resulting in the precipitation from concentrated solutions of a barium and of a lead salt. No quantitative analysis of these salts was given. It was also there mentioned by us that silver nitrate, unlike copper sulphate, does not at once cause decomposition of alkali nitrososulphates. The title of our note is *The Existence of Barium and Lead Nitrososulphates.*

Now, in introducing the account of his preparation of barium-potassium and silver-potassium nitrososulphates, Hantzsch does indeed refer to that note, but only to say that, according to us, salts of the heavy metals cannot be prepared; thus, actually reversing our statement, and leaving unmentioned the above results of our work.

A new point about nitrososulphates which, small in itself, may yet prove of significance in settling their constitution, is that their

aqueous solution becomes strongly alkaline to litmus, phenolphthaleïn, or rosolic acid, soon after alcohol is added to it. No effervescence on standing, otherwise a marked phenomenon, is then observable, and the disappearance of the salt is greatly retarded, probably as an effect of the alkalinity induced in the solution, possibly also through presence of the alcohol itself. Neither sulphite, nitrite, nor oximidosulphonate is produced.

Both Pelouze and Hantzsch describe potassium nitrososulphate as being perfectly neutral to litmus. In this we differ from them. It is so towards phenolphthaleïn and to rosolic acid, but to litmus, almost upon first contact with it, the moist salt is alkaline, and so also is its dilute solution in a few seconds. The salt tested by us had, in one case, been four times recrystallised from pure water. Besides, when the salt, which had proved itself of alkaline reaction, had all decomposed, slowly in the cold, or more quickly at a boiling heat, or in the cold by contact with spongy platinum, the product was always quite neutral potassium sulphate, thus showing the absence of alkaline impurity in the original salt.

The knowledge of the constitution of the nitrososulphates seems to stand just where it did ten years ago, when we were led to see in these salts the presence of the radical—SO_2OK, a view which has met with general recognition since, except for some hesitation about it on the part of Michaelis (*Graham-Otto's Anorg. Chem.*, **4**, 1515). Raschig in adopting it, two years later, fully stated that it was ours, but Hantzsch, in referring to Raschig's views and retaining only that part of his formula, has overlooked that fact. In proposing at that time, a new formula for these salts, we did not venture to resolve the nitroxy-radical, and wrote $K(N_2O_2)SO_3K$, just as Traube is temporarily doing with his isonitramines. At the present time, we are disposed to adopt, as the legitimate outcome of the reduction of these salts into hyponi-

trites and sulphites, the expanded formula $K{\cdot}ON{\cdot}NO{\cdot}SO_3K$, according to which nitrososulphates are simple sulphates of the radical, $M{\cdot}ON_2$— (where M is a univalent metal or ammonium).

There are three objections which can be raised to this conception of their nature. One, made by Pelouze sixty years ago, may be stated almost literally in his words. Is it probable that nitrous oxide, contained as such in these salts, can, by the small rise of temperature upon which it becomes nitric oxide, take oxygen from such a stable compound as sulphuric acid ? We reply that, since the oxygen which has converted sulphite to sulphate has not, in doing so, parted with the nitrogen of the nitric oxide, it may well enough be expected to keep it when, by a sufficient elevation of temperature, the complex molecule of the salt has to break up, though even then, as at lower temperatures, some of it does leave nitrogen in order to remain in the sulphate.

Another objection which may suggest itself, as it also did to Pelouze, to these salts being sulphates, is that they give no precipitate of sulphate with barium chloride. But this may only show that they resemble alkyl sulphates, such as the sulphovinates ; whilst the instantaneous precipitation of barium sulphate on addition of an acid confirms the view as to their sulphate constitution, since all known sulphazotised salts of the sulphonic type take a notable time to begin to precipitate barium sulphate when acidified, brief though that time may be in the case of the trisulphonated nitrile salts, during which hydrolysis is taking place.

A third and obvious objection to the view that nitrososulphates are true sulphates is that they resist decomposition by alkalis. It is here admitted that a constitution in which nitrogen is shown in direct union with sulphur would furnish, *prima facie*, a more satisfactory ground for their stability than one in which it stands only in

oxylic union with the sulphur. However, it should be considered that potassium ethylsulphate, for example, shows some of that stability, characteristic of potassium ethylsulphonate towards alkalies, although in it also there is not immediate juxtaposition of ethyl to sulphur. But the special point for consideration is one which structural formulæ fail to indicate, as in so many other cases. To take the commonest and simplest example, structural formulæ fail to account for the fact that the hydrogen of HO·K is so different in its chemical relations from that of $HO{\cdot}NO_2$. The point, then, is that, because sulphur is bibasic in nitrososulphates as in sulphites and sulphates, potassium nitrososulphate is a salt quite stable towards potassium hydroxide, though extremely unstable towards acids. The sulphur acts, so to speak, through or across the dinitrosyl, upon the potassium just as it acts in sulphates across the intervening oxygen, or as chlorine acts across oxygen as a monobasic radical in chlorates, or phosphorus in phosphates as a tribasic radical.

That nitrososulphates should decompose into sulphates and nitrous oxide, and also by sodium be reduced to hyponitrites and sulphites, is made very evident by the constitution here given to them.

Hantzsch's formula for these salts, $KON{\overset{O}{\wedge}}NSO_3K$, is perhaps preferable to ours for accounting for the stability of nitrososulphates towards alkalis. On the other hand, it affords no explanation of their instantaneous decomposition by acids, while their reduction by sodium becomes a very complex matter. Raschig's formula, $ON{\cdot}N{<}^{OK}_{SO_3K}$, would be almost equally good, were it not designed to show a possible decomposition into oximidosulphonate and nitrous oxide.

Traube (*Berichte*, **27**, 1507) thinks there is analogy between his isonitramines and the nitrososulphates, but we doubt very much that

any substantial analogy will be established between them. It is true that both classes of compounds are metallic salts formed from nitric oxide, but then, as Traube has already shown, one of the nitrogens is united to the alkyl radical of the isonitramine, whereas as we have just pointed out, what little evidence there is shows that one of the atoms of oxygen, and not of nitrogen, is directly united to the sulphuryl of the nitrososulphate. Again, in the formation of nitrososulphates, nitric oxide simply combines with a salt, while in that of isonitramines it unites a salt with more metal. In the formation of nitrososulphates the presence of alkali, essential in the case of isonitramines, may be dispensed with, as was even recognised by Pelouze as regards the ammonium salt, and as has been more conclusively ascertained by us in the case of the potassium salt.

Sodium nitrososulphate.

By

Edward Divers, M. D., F. R. S., Prof.,

and

Tamemasa Haga, F. C. S., *Rigakuhakushi,* **Assist. Prof.**

College of Science, Imperial University.

Pelouze (*Ann. Chim. Phys.*, [2], **60**, 151; *Ann. Pharm.*, **15**, 240) in attempting to prepare sodium nitrososulphate, found it to be far more soluble than potassium or ammonium nitrososulphate, and therefore difficult to prepare. As its general properties, in solution, seemed to be the same as those of the potassium salt, he did not proceed to isolate it or to examine it further.

The potassium and ammonium salts crystallise out when a fairly concentrated solution of the respective sulphite, along with some excess of alkali, is submitted to the action of nitric oxide. This is not the case with the sodium salt, which can only be obtained by evaporating the solution left by the action of nitric oxide upon sodium sulphite. We obtained it by exposing for five days at about the mean temperature, to an atmosphere of nitric oxide, a very concentrated solution of normal sodium sulphite, to which had been added, as a preservative, one-fortieth of its weight of sodium hydroxide, and which was contained, to only a shallow depth, in a connected series of Erlenmeyer flasks. For half this time the gas was under the additional pressure of a column of water, and for the rest of the time at the barometric pressure only.

The flasks were occasionally shaken, but as no incrustation of the solution occurs in this case, agitation was less useful than in making the potassium or ammonium salt.

At the end of the time, the solution was showing slight effervescence, indicative of decomposition going on in the salt. Hardly any sulphite then remained, and nearly all of what sulphate had formed or been present at starting was crystallised out by keeping the solution for some time at a little below zero, and then removed. The solution was quickly evaporated in a vacuum desiccator to a very small volume, by which time it had yielded much of what proved to be nitrososulphate, in opaque white crusts and deposits of minute hard crystals, perfectly transparent under the microscope. Removed to the porous tile and drained dry, the salt formed a crystalline powder, tasting remarkably like common salt, slightly alkaline to litmus, and free from sulphate and sulphite. It was weighed and then left for a night in a desiccator, to see what it would lose in weight as moisture and water of crystallisation. Next morning, it appeared to be unchanged, and was placed on the balance-pan, between watch-glasses. But it could not be weighed, because it rapidly lost weight. Taken from the balance and uncovered, it had not been a minute exposed to the air before it began to have a nitrous odour, and then quickly grew very hot and evolved much nitrous oxide mixed with nitric oxide, which reddened in the air. The watch-glass which held the salt was broken, and the wood of the table scorched, on which it rested. The powdery solid residue was collected, with hardly any noticeable loss, and weighed.

This residue of the decomposed salt consisted of sulphate and sulphite, and weighed, as collected, 5·645 grams, while the nitrososulphate, as placed in the desiccator, had weighed 7·595 grams. In portions of the residue we determined its sodium by ignition with

sulphuric acid; its sulphur by oxidation with bromine-water and precipitation with barium chloride; and its sulphite by titration with iodine. These were all calculated as parts per cent. of the salt before it was placed in the desiccator. The numbers found show a deficiency of about 3 per cent. from those for the anhydrous salt, while sodium nitrososulphate with one mol. of crystal-water would have lost 8·8% in becoming anhydrous. Here are the tabulated numbers:—

	$Na_2N_2SO_5$.	Found.	$Na_2N_2SO_5$ with 3% deficient.
Sodium	24·73	24·13	23·99
Sulphur	17·20	16·64	16·68

This deficiency includes moisture and any solid particles carried away during the very rapid evolution of gas by the salt when decomposing. From the weight of the residue and that of the sulphite it contained, it can be calculated, approximately at least, that about 1·6% of the original salt, or 1·2% of sulphate and sulphite, were mechanically lost by the decomposition of the salt, and, therefore, that, when placed in the desiccator, it had contained about 1·4% of moisture. Now, the amount of sulphite in the residue was 9·8% of it, or 7·28% of the damp nitrososulphate. Therefore, to recompose the salt, we have—

Sodium sulphite	7·28
Nitric oxide eqvt. to this	3·47
Sodium sulphate	67·05
Nitrous oxide eqvt. to this.....	20·78
Moisture, by difference	1·42
	100·00

Sodium nitrososulphate is, therefore, an anhydrous salt, like the potassium salt. Like the potassium salt, also, though it continuously decomposes into sulphate and nitrous oxide when in neutral solution,

it can be heated moderately with very little change, if some sodium hydroxide is present. But when such an alkaline and somewhat concentrated solution is boiled, it rapidly decomposes into sulphite and nitric oxide, and this the potassium salt does not do.

It thus seems that the reversion of nitrososulphates to nitric oxide and sulphite is dependent upon temperature alone and is not prevented by the presence of water. It is otherwise with their decomposition into nitrous oxide and sulphate, which is caused either by water alone, or by elevation of temperature alone. For at the common temperature they can be kept for an apparently indefinite time when dry, but decompose in damp air or in solution, while when heated, even in dry air, they generally decompose much more in this way than into nitric oxide and sulphite. One exception to this is the potassium-silver salt, which when heated gives only nitric oxide and sulphite (Hantzsch). This fact points to the latter decomposition as the primary effect of heat in all cases, and to the production of sulphate and nitrous oxide as the result of interaction of nitric oxide and sulphite. Potassium-silver sulphite not being readily oxidisable, this interaction does not occur when potassium silver nitrososulphate decomposes.

The Constitution of the Nitrososulphates.

By

Edward Divers, M.D., F.R.S. Prof.,

and

Tamemasa Haga, F.C.S., *Rigakuhakushi,* Assist. Prof.

College of Science, Imperial University.

Following up the fact we have already made known (this vol., pp. 91, 92), that an aqueous solution of potassium nitrososulphate becomes strongly alkaline soon after the addition of alcohol to it, we have got results which seem to supply all that was wanting to bring our knowledge of the constitution of the nitrososulphates up to the standard of the present state of chemistry.

Some chemists have recently (*Berichte.* **27**, 1508; 3264; 3498), allowed themselves to call these salts *nitroxysulphites*, a name which points to the fact that they are produced by the union of nitric oxide and a sulphite, but ignores all else concerning them, ascertained even at the time of their discovery. Pelouze, in 1835, showed a keener appreciation, than these chemists of to-day here display, of the nature of chemical union, and called them *nitrosulphates.* According to him, they are not sulphates, ordinary sulphates that is, for they do not precipitate barium chloride (unless acidified), but are complex salts, substituted sulphates, as we should now say. Watts, in his *Dictionary*, adopting Pelouze's view, modified the name to *nitrososulphates*, in order to distinguish these salts from *nitroxyl* compounds.

After oxygenous salts had come to be regarded as oxylic compounds, sulphites were formulated as $SO(OM)_2$, in which M is symbol for a univalent basic radical, and in accordance with this, E. Frankland (*Lecture Notes*, 1866) expresed the sulphatic constitution of Pelouze's salts by the formula, $(NO)_2{:}SO(OM)_2$, that is, he considered the sulphur to become hexavalent by uniting with two nitric-oxide radicals, in place of the atom of oxygen taken up by sulphites in oxidising. Later on, as it became evident that inorganic sulphites were of one class with organic sulphonates, and that sulphites, sulphates, and thiosulphates are best formulated as $M{\cdot}SO_2{\cdot}OM$; $MO{\cdot}SO_2{\cdot}OM$; and $MS{\cdot}SO_2{\cdot}OM$, respectively, it was seen that, by analogy, nitrososulphates had to be written, $M(N_2O_2)SO_2{\cdot}OM$, in which change of valency is no longer exhibited. This view of the constitution of nitrososulphates and of their relation to sulphites was advanced, some ten years ago, by us (*J. Ch. Soc.*, **47**, 203; see also **47**, 218).

The facts on which this view of the constitution of nitrososulphates, so far as it goes, rests, seem amply sufficient. First, there is the production of the nitrososulphates in a way precisely analogous to that of sulphates and thiosulphates from sulphites, namely, by leaving a solution of a normal sulphite in contact with nitric oxide, oxygen, or sulphur, as the case requires. Then comes the reversion of nitrososulphates to nitric oxide and sulphites: not only do they, when heated in the dry state, thus decompose (Pelouze)—wholly in the case of silver-potassium nitrososulphate, partly in other cases (Hantzsch)—but sodium nitrososulphate does so even in hot solution (see preceding paper). For this behaviour is in full agreement with what has long been known of the thiosulphates, notably of the calcium salt, which, in the first place, is producible by digesting calcium sulphite and sulphur with water, at a gentle heat, and, then, is decomposable into these substances, by boiling its concentrated solution. Lastly, sodium

amalgam acts alike upon solutions of nitrososulphates and thiosulphates, hyponitrite or sulphide being formed, along with sulphite in either case.

What precedes refers only to the relations of the nitric oxide, as a whole, to the rest of the nitrososulphate. There remain to be considered the relations of the elements of the nitric oxide to each other and to the sulphuryl and adjacent basic radical or metal. Putting together the constitution of hyponitrites as established by Zorn, and the generation of these salts from nitrososulphates observed by us, nitrososulphates might long ago have been formulated as $MON_2O{\cdot}SO_2{\cdot}OM$, as indeed was done by Michaelis in entering our results in his edition of *Graham-Otto's Lehrbuch*, but which we had hesitated to do. On the other hand, Raschig, W. Traube, Hantzsch, and Duden consider nitrososulphates to be sulphonates, from analogies which we do not find to hold good, for reasons already given in our previous paper. We have, there, also expressed preference for the sulphate constitution of these salts, on the ground that they instantly and fully give the reaction of a sulphate, upon addition of barium chloride acidified with hydrogen chloride, since even the least stable of the certainly sulphonic nitrogen compounds, discovered by Fremy, take an appreciable time to begin precipitating, and a not inconsiderable time to finish doing so. To make this difference in behaviour more assured, we have thoroughly tested, by heat under pressure, the mother-liquor of barium sulphate just precipitated from potassium nitrososulphate, and have found no residual sulphur in it.

That nitrososulphates are not sulphonates, but true sulphates, we can now finally establish through the effect of alcohol upon them in aqueous solution. Alone in solution, the potassium salt slowly decomposes into normal sulphate and nitrous oxide, but when a little alcohol is present, it partly changes into potassium ethyl sulphate,

potassium hydroxide, and nitrous oxide, thus:—

$$(KON_2)KSO_4 + EtOH = EtKSO_4 + KOH + N_2O.$$

Potassium hydroxide and nitrous oxide are what potassium hyponitrite becomes, when left dissolved in water, and may here be taken to have been derived in that way, although, as a matter of fact, we have failed to detect any hyponitrite in the solution at any period in the decomposition of the nitrososulphate. For this failure presents no difficulty, since potassium hyponitrite in solution decomposes quite as quickly as it can here be produced. We may, therefore, express the interaction of alcohol and nitrososulphate by the equation—

$$(KON_2)KSO_4 + EtOH = EtKSO_4 + KON_2OH$$

—KON_2OH being the acid hyponitrite, existence of which in solution was established by Zorn.

Whether hyponitrite or only alkali and nitrous oxide are the other products, the fact that potassium ethyl sulphate is formed removes all doubt as to nitrososulphates being true sulphates. Were they of sulphonic constitution, they could only yield ethyl sulphate along with hydroxylamine, hydrazine,* or ammonia, or a derivative of one of these, and then by a most improbable reaction. No such substances are found as products of the decomposition.

Nitrososulphates having thus been ascertained to be true sulphates, the relations of the elements of the nitric-oxide radical can be only those shown by the formula, $MON{:}NO{\cdot}SO_2{\cdot}OM$. For there is nothing in the gentle act of union of the nitric oxide with the sulphite suggesting any new distribution of its elements, such as that of the oxygen of one mol. of the nitric oxide leaving it to go over to the nitrogen of the other; nothing in the properties of the nitrososulphates

* Duden has recently found that potassium nitrososulphate yields some hydrazine with sodium-amalgam (*Berichte*, **27**, 3498). It, therefore, seems probable to us that what has been taken by Maumené, ourselves, and others, to be hydroxylamine among the products of the action of sodium upon nitrites, is, after all, not that substance but hydrazine.

pointing to the presence in them of the nitroxyl radical; nothing probable in the supposition that, in their formation, the metal or basic radical quits the sulphur of the sulphite for the nitrogen of the nitric oxide rather than for its oxygen. On the contrary, there are the facts that metallic sodium, when it acts upon them, finds in them the hyponitrite radical, (though possibly, indeed, making it for itself), and leaves sulphite; and, again, that they are almost neutral to litmus, instead of being strongly alkaline, as they likely would be, if their metal were in direct union with the nitrogen. The hyponitrite-sulphate formula displays every known chemical property of them, whereas a sulphonic formula displays only some of these, and suggests the existence of properties which they do not possess, such as that of hydrolysing into a hydrogenised nitrogen compound.

The great rise of temperature which attends the dry decomposition of a nitrososulphate into metal sulphate and nitrous oxide must be attributed rather to the heat of nitric oxide decomposing into nitrous oxide, than to the oxidation of sulphite, since this is already, in the salt united to oxygen.

Nitrososulphates may be described as anhydro-double salts of hyponitrous and sulphuric acids which in aqueous solution hydrolyse into acid-hyponitrite and acid-sulphate, these salts simultaneously changing into normal sulphate and hyponitrous acid (nitrous oxide and water), thus:—

$$OH_2 + O\left\langle\begin{matrix} N{:}NOK \\ SO_2{\cdot}OK \end{matrix}\right. = N_2\left\langle\begin{matrix} OK \\ OH \end{matrix}\right. + SO_2\left\langle\begin{matrix} OH \\ OK \end{matrix}\right. = N_2O + OH_2 + SO_2(OK)_2.$$

The property they show of never exchanging their nitroso-metallic radical for a simply metallic one, when they are mixed in aqueous solution with other salts, is apparently nothing more than what is seen in the true sulphate, potassium-ethyl sulphate. In this

connection, it is very interesting to see the nitrososulphate exchanging its specific radical for an alkyl radical and thus becoming potassium or other ethyl sulphate; also to see alcohol acting as a hydroxide upon an alkali sulphate. And then, along with this as a consequence, comes the most remarkable thing of all, that by submitting potassium sulphite to the action of nitric oxide and alcohol, it becomes possible to generate potassium hydroxide. That alcohol can directly give rise to potassium hydroxide by acting upon any potassium salt, seems an impossibility, and this furnishes a strong argument for believing that its real action upon potassium nitrososulphate is what we have assumed it to be, namely, the formation of acid potassium hyponitrite, which then decomposes with water and gives the hydroxide.

The constitution of nitrososulphates, now established, shows that these salts have nothing in common with the sulphazotised salts of Fremy, which are all sulphonates, and that they have some relation to the nitrosyl sulphates.

Experimental examination of the action of alcohol upon nitrososulphates.

Potassium nitrososulphate, in fine powder, was sealed up in a tube with absolute alcohol, and kept at 100° for some hours. The two substances had no action on each other.

Some preliminary experiments made the production of potassium ethyl sulphate from an aqueous solution of potassium nitrososulphate and alcohol almost a certainty, and also enabled us to obtain in the solid state some potassium carbonate, in proof that potassium hydroxide had formed, and had subsequently become carbonated by long exposure to the air. We then made two experiments, which we here describe in full, intended partly to be quantitative, but principally

to afford us sufficient potassium ethyl sulphate in a pure state, for thorough identification. In one experiment we prepared a solution containing 46·25 grams of potassium nitrososulphate in 1450 grams of 22·8 per cent. spirit, and in the other, 14·45 grams of the salt in 212 grams of 14 per cent. spirit. Both solutions were almost saturated; we had intended the one to be spirit of 25°/₀ alcohol and the other of 15°/₀ alcohol.

The solutions were left for 16 days, at the summer temperature in loosely stoppered bottles, though a few days less might have sufficed for the decomposition of the salt to be complete. Potassium sulphate gradually crystallised out and nitrous oxide slowly escaped. In our first paper on the subject in this volume, we stated (p. 92) that the evolution of nitrous oxide from the aqueous solution was actually arrested by adding alcohol; but that was a mistake. It goes on undiminished, but, being spread over a much longer time, becomes much less perceptible. We also observed a slight but unmistakable odour of aldehyde during the decomposition, and were just able to reduce silver by it in the solution (the alcohol used being quite free from this impurity). Its formation may perhaps be accounted for by supposing a minute quantity of the nitrososulphate to have decomposed into nitric oxide and sulphite, the former then acting as carrier of atmospheric oxygen to the alcohol.

The volume of the solution of the 46·25 grams of salt being so large, it was reduced to half by evaporating the solution at 70–75° in shallow, flat-bottomed glass pans. The alkali present was then neutralised with volumetric sulphuric acid, the solution made again slightly alkaline, and the evaporation continued and completed in a vacuum over sulphuric acid, occasionally interrupting the process to remove the potassium sulphate that had separated, in order that the quantity of it in the dried-up residue should not be very large in

proportion to the potassium ethyl sulphate. The evaporation of the solution of the 14·45 grams of salt was effected wholly in the desiccator, that is, without the application of heat. Before evaporating, the alkali was almost neutralised with sulphuric acid.

The residue from the larger quantity of salt was extracted at an ice-cold temperature, with 5 ccs. of proof spirit, and that from the smaller quantity with 4 ccs. of proof spirit. In this way almost all remaining sulphate was left insoluble. The spirit solution evaporated gave, in the former case, 2·64 grams of crude potassium ethyl sulphate, and 1·37 grams in the latter. These quantities were necessarily only fractions of the actual quantities produced, because of the very great waste attendant on the separation of much potassium sulphate from the exceedingly soluble potassium ethyl sulphate. A true measure of the extent to which the nitrososulphate had undergone conversion into the ethyl sulphate was, however, afforded by the quantity of potassium hydroxide produced, which was estimated, by titration, in the experiment upon the 46·25 grams of nitrososulphate. It amounted to 1·69 grams, or 3·66 per cent. of the weight of salt taken, or about 14 per cent. of what would have been formed, had the whole of the salt suffered the same change. This 1·69 grams of potassium hydroxide must have been accompanied by 4·95 grams of potassium ethyl sulphate, although we isolated little more than half that quantity, namely, 2·64 grams.

In proportion to the amount of salt taken the yield is $1\frac{2}{3}$ greater where the 14 per cent. spirit was used, than where 24 per cent. spirit was used. The difference is sufficiently great to justify the belief that the formation of the ethyl sulphate is actually greater with weaker than with stronger alcohol, in spite of the very imperfect means we took to collect this salt. On first consideration, it may seem that the formation of potassium ethyl sulphate must be favoured by strengthen-

ing the solution in alcohol. But this by no means follows of necessity, for it must be borne in mind that addition of alcohol greatly lessens the power of the water to dissolve the salt. Now, the decomposition of the salt by alcohol is alternative to that by water, but not opposed to it, so that in connection with the reaction with alcohol, the water may be regarded as merely the vehicle for the salt and the alcohol, and then we see that, provided these are present in molecular proportions, more alcohol can only serve to make need for the presence of more water to keep the salt dissolved, since this is not acted upon by alcohol when not in solution. The more water there is present, the more attenuated is the salt exposed to the action of the alcohol. Thus, with 14·45 grams of salt in solution in 212 grams of 14 per cent. spirit, there was twice as much salt in a given volume as there was where 46·25 grams of salt were dissolved in 1450 grams of 24 per cent. spirit, while in both cases the alcohol present was far in excess of one molecule, being even in the dilute spirit nearly ten times the molecular quantity. Even if the chemical activity of the water is considered, still the water is present in much smaller proportion to the salt in the dilute spirit than in the stronger. The matter is an interesting one, but needs more work to be done in connection with it, before anything can be safely concluded about it.

That the salt, which we had obtained, was potassium ethyl sulphate, was ascertained by qualitative and quantitative tests. It was a neutral, exceedingly soluble, somewhat deliquescent salt, forming pearly plates, and giving no insoluble salt with any reagent. A concentrated solution boiled soon contained sulphuric acid; a dilute solution boiled for some time remained free from it. In a solution acidified with hydrochloric acid and boiled, decomposition quickly began but was not complete until the solution had been heated under pressure. When acidified and rapidly heated in a sealed tube to 150°,

it was found to produce a little combustible gas, but when the tube was only slowly heated to 150°, the decomposition was perfect into potassium hydrogen sulphate and alcohol. In all these respects, the salt we had obtained agreed with potassium ethyl sulphate.

For quantitative analysis the salt was re-crystallised from water. Ignited with sulphuric acid it gave potassium sulphate equivalent to 24·09 per cent. potassium. Heated in a sealed tube with hydrochloric acid for some hours at 100°, and then for some hours longer at temperatures rising to 150°, it gave barium sulphate equivalent to 19·09 per cent. sulphur. The filtrate from the barium sulphate, evaporated to dryness and fused with potassium hydroxide, gave no additional sulphur. The alcohol formed by the hydrolysis of the salt was distilled off and easily identified as such by its odour and taste, and by the iodoform and aldehyde tests; but no attempt was made to estimate its quantity. The calculated amounts per cent. for potassium ethyl sulphate are potassium, 23·83, and sulphur, 19·52, with which our finding sufficiently closely agrees.

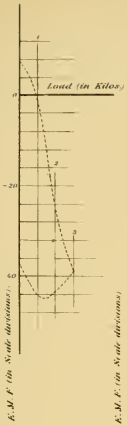
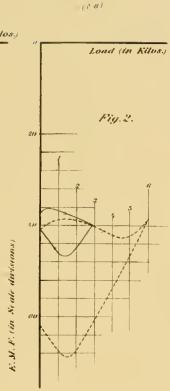


Fig. 1.



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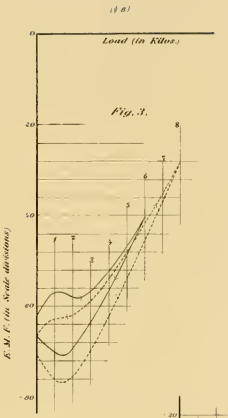

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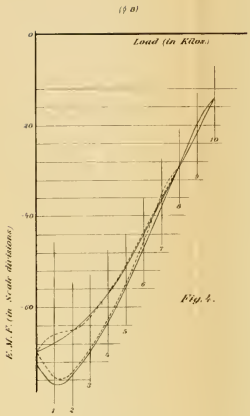

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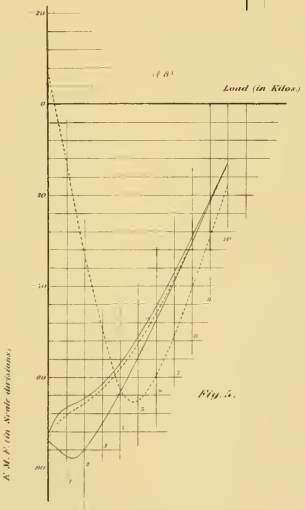

Fig. 5.

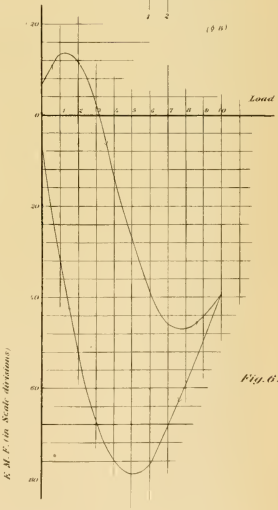

Fig. 6.

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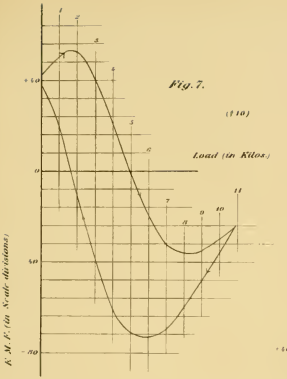


Fig. 8.

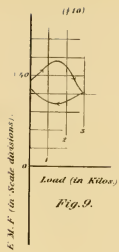
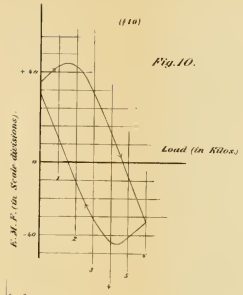
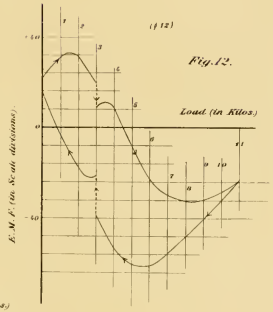
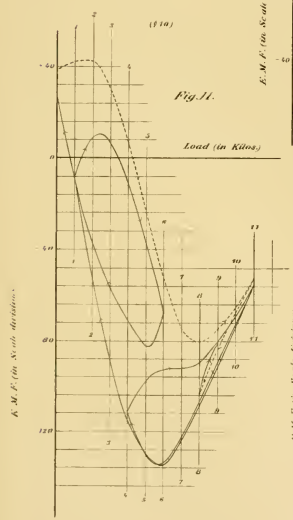
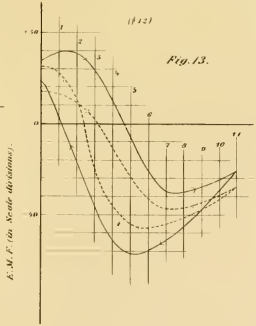


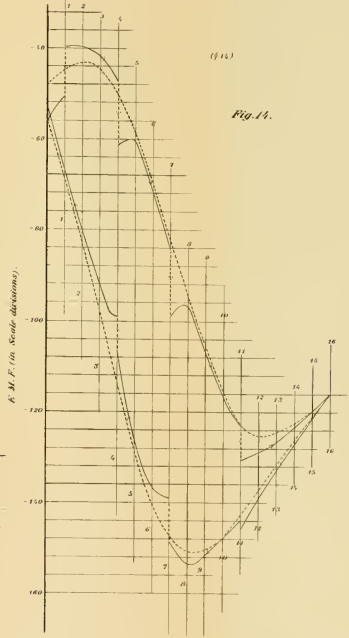
Fig. 9.











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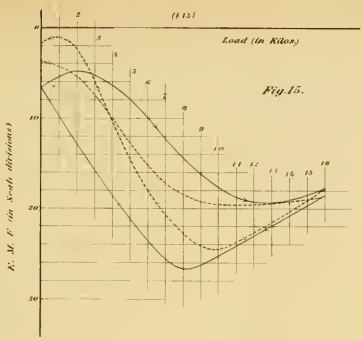

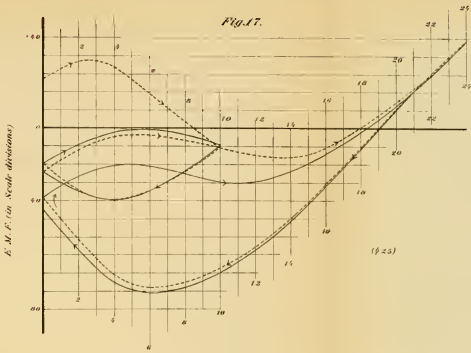

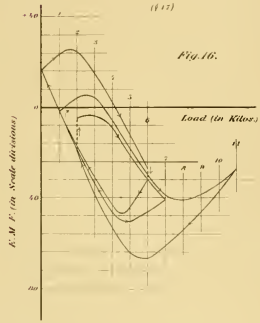

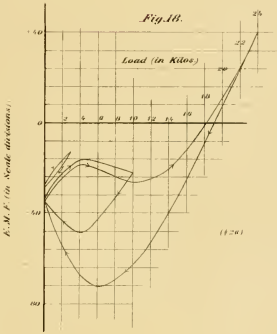

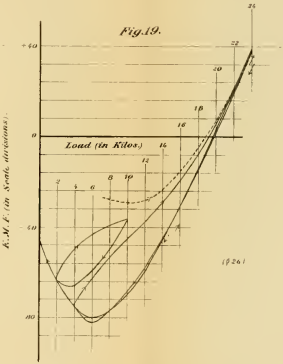

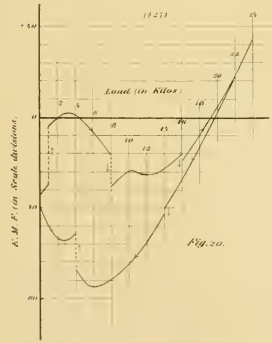

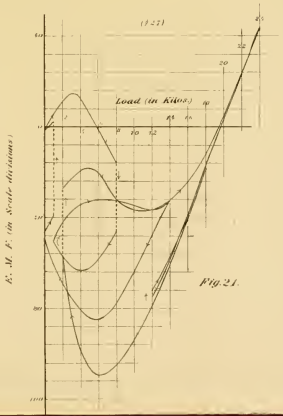

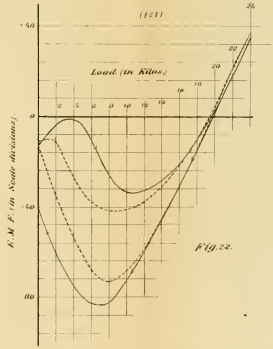

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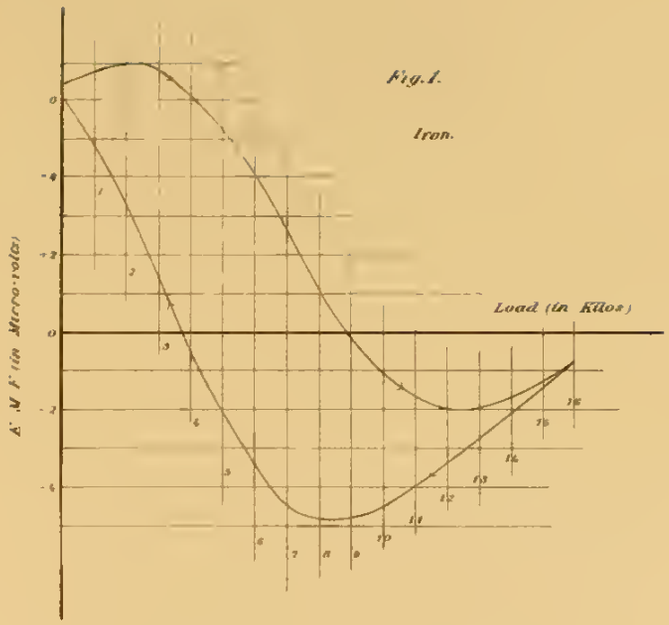
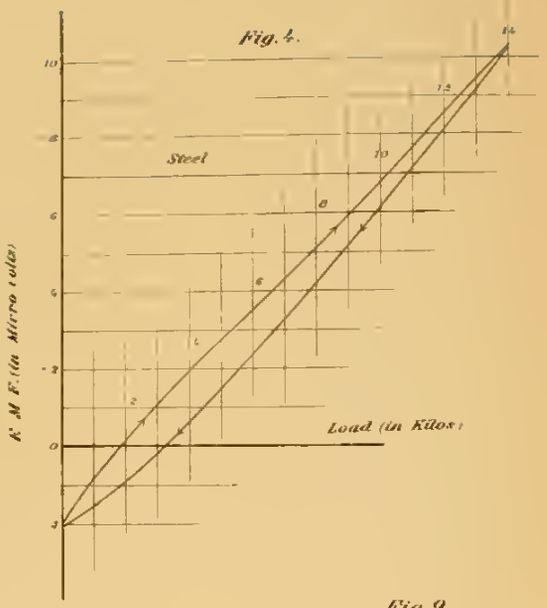




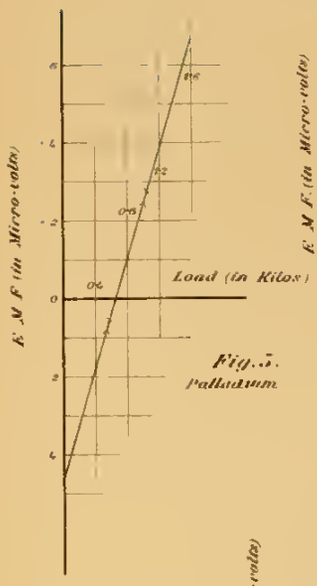


Fig. 5.
Palladium

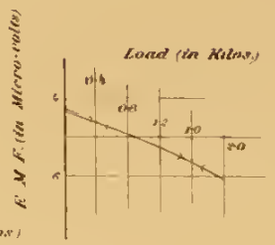


Fig. 8.
Silver

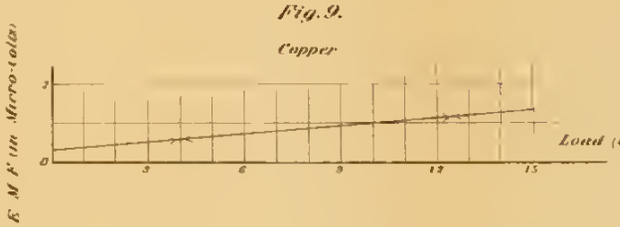
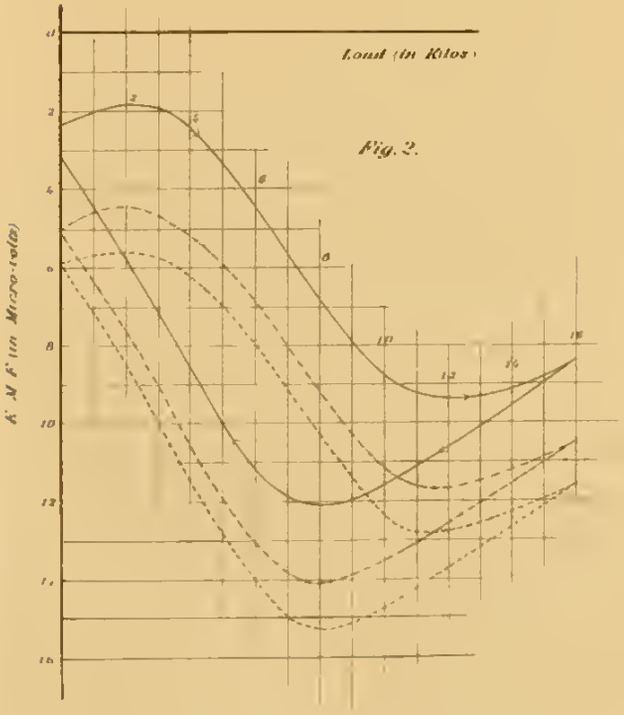
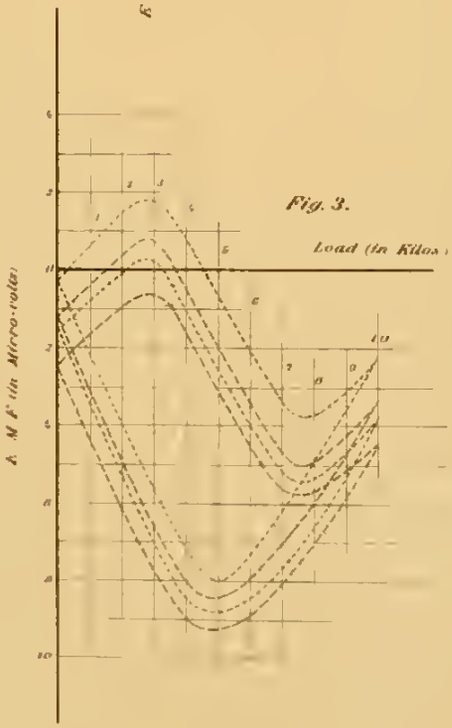


Fig. 10.
Aluminium





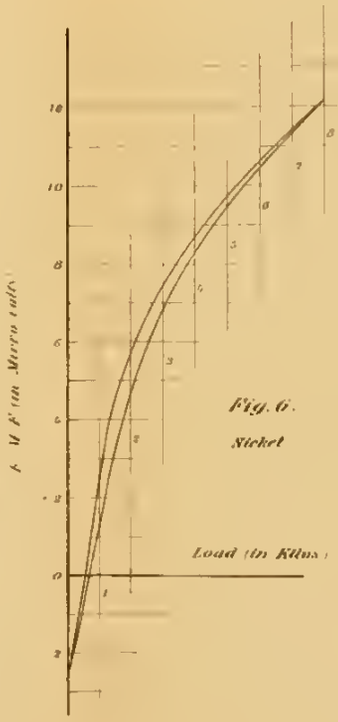


Fig. 7.
Platinum

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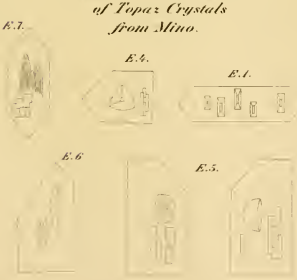
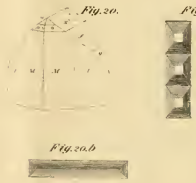
Topaz Crystals from Mino.

Natural Etched Figures of Topaz Crystals from Mino.



Topaz Crystal from Oui.



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The Tinfoil Grating Detector for Electric Waves.

By

T. Mizuno, *Rigakushi.*

Professor of Physics, First Higher School.

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§ 1. In a paper,* which not long since I communicated to this Journal, I suggested that the change of the resistance of the grating might be due to a mechanical effect exerted upon it by impinging trains of electric waves. In other words, electric waves might give impulses to some of the strips of the grating in such a way as to let leaflets on their margins come in contact with one another, thereby causing a diminution of resistance. In order to confirm this view, further inquiries were carried out soon after the communication of the above mentioned paper.

§ 2. Having constructed about forty gratings and tested their action, I found to my surprise that while some were extremely sensitive, others were not, being even utterly indifferent to the impulses of electric waves, although they had all been prepared with the same care and apparently with the same success.

This led me to undertake a closer examination of such gratings, which gave results that throw much light upon their nature. But before these results can be stated, it is necessary to describe in detail my way of preparing the gratings, because upon that their sensibility wholly depends.

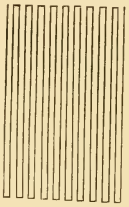
---

* Note on Tinfoil Grating as a Detector for Electric Waves, Vol. IX, Pt. 1, 1895.

§ 3. The face of a flat wooden block of convenient size, say, 10 cm. on a side, was pasted over with very fine tinfoil, as described in my former paper.

Then came cutting lines into the tinfoil, to which particular attention was given. Along the edge of a bamboo ruler a sharp knife, held always inclined away from the ruler, was drawn lightly across the surface of the tinfoil. In this way, many fine parallel slits were cut in the tinfoil, so as to make one continuous, regular, zigzag line, as shown in Fig. I.

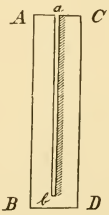
Fig. I.



A few of the gratings, thus carefully prepared, were found to be sensitive. But experience has taught me that success in preparing good detectors depends, to a large extent, upon the nature of the wood block on which the tinfoil is pasted in the first place and next upon the degree of adhesion of the foil to the wood. A soft wood is preferable to a hard one, and the paste used should not be thick enough to make the foil adhere too firmly.

§ 4. The majority of the slits of the sensitive gratings, when examined under a microscope, presented such an appearance as that shown in Fig. II. A B and C D represent two strips of foil with the very narrow slit or gap *a b* between them that has been formed by the knife. The shaded portion indicates the slope of the tinfoil found at one edge of each strip.

Fig. II.



For the sake of clearness, there is shown in Fig. III., an end view, that is, a section of the two strips perpendicular to their lengths. The shaded portions indicate the tinfoil strips, A B and C D in Fig. II., of which the edge of one strip, C D, extends some

distance into the gap, *a b*, and forms the slope mentioned above. Along this slope the tinfoil presents many folds or wrinkles, which seems to show that the tinfoil strip was somewhat stretched along its edge by the act of cutting it. Non-sensitive gratings, showed none of these characteristic appearances, but had the gap between the strips much wider, with no decided slope and no appreciable folds along the edges of the strips. Hence for a grating to be sensitive, it appears to be necessary that the gaps should be narrow and their margins sloped and in folds.

Fig. III.

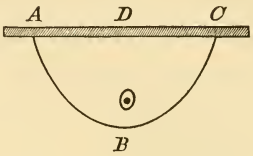
§ 5. Although I have been unable to see clearly the interior of a gap, yet it is quite reasonable to assume that in sensitive gratings there will be numbers of leaflets along the margins of adjacent tinfoil strips ; and the existence of such leaflets once admitted the explanation of the action of the gratings becomes clear. For, in a properly constructed grating some of the leaflets may easily come in contact with one another under the action of the electric waves, because of the extremely small distance between any two opposite leaflets in the narrow gap. Then, too, it seems to me that these leaflets must be of various dimensions and, accordingly, some of them will be extremely sensitive, others less so but still highly sensitive, others again only moderately so. This being the case, the amount of change in the resistance of the grating must depend upon the intensity of energy of the impinging electric oscillations, for, when it is not great enough, only the most sensitive leaflets will come into play, but when it is sufficiently great all the effective leaflets will be brought into action. All the experiments I have yet made are in agreement with this representation of the matter.

§ 6. A grating, well prepared so as to fulfil the conditions mentioned above, proves to be an extremely sensitive detector for

electric waves as will be seen from the experiments which I now describe.

Experiment 1: A Hertzian parabolic vibrator, ABC, was placed horizontally with aperture turned upwards, as shown in Fig. IV. The aperture was covered with a sufficiently large wooden plate, A D C, entirely coated with tinfoil. A grating, whose initial resistance was about 71 ohms, was placed at about 5cm. from the plate and in a vertical line with the primary conductor, O, radiating electric waves of 60 cm. wave-length. Then, exciting the primary oscillations, I always found that the resistance of the grating was diminished by from 1 to nearly 2 ohms.

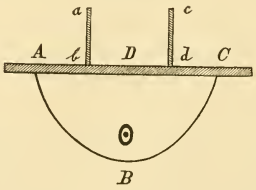
Fig. IV.



The experiment was repeated after raising the plate, ADC, parallel to itself and keeping it at some height from the aperture, A C. Similar changes of resistance were also observed in this case. This phenomenon may of course be understood by considering the fact that some electric waves, which pass out of the uncovered portions of the parabolic vibrator, will, after going through the room and being reflected from the surrounding walls, ceilings, &c., come back ultimately to the grating in a much enfeebled state.

Experiment 2: The above experiment was modified by placing on the plate, A D C, a zinc box, *a b c d*, 17 cm. by 27 cm., without top or bottom and putting the grating inside it. In this case also, a change of resistance, was observed though smaller. It is then certain that although the side effects were got rid of, the top effect still remained, through which traces of waves might affect the resistance of the grating. The

Fig. V.



fact that we can annul the change of resistance by completely closing the top of the box with a metallic plate seems especially to favour the above explanation.

Experiment 3: The grating was connected with the Wheatstone's bridge by means of two leading wires, and at the same time placed inside the zinc box, just as in Exp. 2. After balance had been well established and the top of the box closed, the primary oscillations were excited. This time, the balance was at once destroyed and the resistance of the grating showed an appreciable diminution, in spite of the fact of the grating being wholly enclosed in a metallic box. Taking away one of the leading wires the phenomenon yet remained the same, though the change of resistance seemed somewhat smaller than in the former case. The leading wires thus appeared to catch up electric oscillations and guide them to the grating. Hence in experiments with electric waves it is necessary to keep the grating free from any exposed wires, which might easily take up electric disturbances. Such effects due to leading wires were observed also by Herr Aschkinass during his researches with these gratings.

§ 7. To what extent the sensibility of the grating reaches will now be quite clear from the results of the above experiments. It is next of great importance to describe some experiments as to the variation of the sensibility. In its primitive state, the grating properly constructed is so sensitive that it can detect even the smallest electric oscillations. But after having been used a few times, its sensibility undergoes a sudden and decided diminution, and then remains nearly constant. At first, when the grating is exposed to electric waves and its resistance consequently diminished, a single tap given to it is almost enough to restore the resistance to its initial or primitive value. But when we have used the grating repeatedly,

we find it necessary to give it a greater number of taps to effect this restoration. Later on, when the sensibility has diminished to a certain value, it seems to retain that value without any decided further change for a long time. This variation in the sensibility may be accounted for in the following way. As mentioned in § 5 the effective leaflets along the margins of the several tinfoil strips may be of different sizes, and some of them possibly very small. The smaller the leaflets the more sensitive to electric disturbances and consequently the more liable to fatigue will they be. Hence in the primitive state such leaflets are easily affected by even very weak electric impulses, but soon lose this sensibility as a result both of the repeated electric disturbances and of the mechanical taps given to them each time.

§ 8. Though the sensibility of the grating thus always diminishes to a certain extent by a little use, still it is even in such a state far superior to that of an ordinary Hertzian resonator. Even where the latter fails, the grating always shows the presence of electric waves if there be any. Experiments on the nature of electric waves, namely, on rectilinear propagation, reflection, refraction, diffraction, polarisation, &c., can all be easily carried on by means of a properly constructed grating. Moreover, such a grating gives not only qualitative, but also quantitative results, to a certain extent, because the amount of diminution of the resistance depends upon the quantity of energy of the impinging waves. Hence, I believe, it may prove to be of great advantage to make use of such gratings in all lecture experiments as well as in laboratory researches on electric waves.

In conclusion I wish to express my thanks to Mr. U. Takashima for the kind and earnest assistance he has given me in the preparation of many of these gratings and in carrying out researches upon them.

On the Piedmontite-rhyorite from Shinano.

By

N. Yamasaki, *Rigakushi.*

College of Science, Imperial University.

With Plate VI.

The occurrence of piedmontite in Japan is well-known, on account of its presence as an essential ingredient of a crastalline schist in the Sambagawa series, which is pretty widely developed throughout the country.* But this mineral had not been met with in other rocks within the confines of the Japanese islands, before I found it recently in the rhyolite from Shinano, a province lying to the north-west of Tōkyō.

The north-eastern part of the Shinano highland consists chiefly of the tertiary formation, through which penetrate various kinds of effusive and dyke rocks. Among them, andesite plays the principal *rôle*, while the others occur, here and there, in comparatively small patches. On the eastern side of the Chikuma, the largest river in the main island (Hondo), and near the well-known cocoon market, Ueda, there is a small range nearly 12 kilometres long, rising about 1300 metres above sea-level. It runs north-south, or nearly paralled to that river. The eastern flank of the range hangs over the Sochi valley, through which a tributary of the Chikuma runs southwards. The greater part of this range is built up of the younger tertiary

* B. Koto, *Some Occurrences of Piedmontite in Japan.* Jour. Sci. Coll., Imp. Univ., Tōkyō. 1887, vol. I. p. 303.

formation, and rhyolite and propylite (apo-andesite) make their appearance through it. The principal rocks of the tertiary strata are shale and coarse, green, tuffogenic sediment. The former, which is generally the older, is well developed in the northern part of the district, and the latter in the southern part. Sometimes, however, one occurs interstratified with the other in thin layers. The direction of strike runs S–W to N–S, with slight deviation in some places. A special geological feature of the sedimentaries can be seen in connection with a large mass of rhyolite in the centre of the district, where the igneous rock covers the tertiary shale at the foot of the Djizo-pass, while on the western part of the range, it is covered by the shale. Besides the large mass of rhyolite there are also small dykes of it, some good exposures of which are easily recognisable in the railway-cutting along the Chikuma river, even from the passing train. The shale in contact with the igneous rock is in general much hardened and assumes a somewhat flinty aspect.

The geology of this district becomes clear from the fact that the large mass of rhyolite takes the form of laccolite, like that of the Henry Mountains, described by Gilbert.* It was once covered by the sedimentaries, since eroded away, and leaving the hard internal core exposed at the surface. The laccolitic rhyolite crops out in the Soehi valley where it forms precipitous cliffs in some places, exhibits a beautiful wavy-jointed structure, well seen on the western precipice of the valley, and usually contains much common epidote. But the locality where the typical piedmontite-rhyolity appears, is one limited to a small area at Karuizawa-shinden (not the village of the same name on the Usui-pass), at the upper end of the Soehi valley, about 10 kilometres north from Ueda, and not far from the Sakaki station.

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*G. K. Gilbert, *Report on the Geology of the Henry Mountains*, 1877, quoted in Neumayr, *Erdgeschichte*, I, p. 177.

Megascopically, the piedmontite-rhyolite is a light-coloured, compact rock of trachytic appearance. The ground-mass is dull-white and encloses phenocrysts, or grains of feldspar and quartz, besides many small aggregates of common grass-green epidote and cherry-red piedmontite. Some of the aggregates look like porphyritic crystals, but on close observation are seen to be really assemblages of minute crystals which have replaced certain original crystals, or occupy fine fissures or drusy cavities of varying size. In some large cavities the aggregate consists of beautiful fine needles of piedmontite radially arranged.

Under the microscope, the rock is seen to be decomposed through weathering. The micro-holo-crystalline ground-mass, which is a plexus of fine grains of feldspar and quartz, is thoroughly clouded with greyish-brown decompotition products of its own, as well as of those of the porphyritic crystals. The outline of quartz, which occurs in both macro- and micro-porphyritic grains, is rounded in all cases by the corrosive action of the magma. Indentations of the ground-mass into the quartz are not infrequent ; sometimes, many of them are found in a single grain, as shown in Fig. 2. Gas-inclusions are rare, and when found have usually a linear chain-like arrangement.

Feldspar occurs in the two forms of orthoclase and plagioclase. The former, less in quantity than the latter, is commonly lath-shaped and often exhibits the Carlsbad twinning. The plagioclase is twinned after the albite-type. Both feldspars are more or less kaolinised through decomposition and there is no crystal which is not thus changed. When highly decomposed, the whole of the crystal is stained of a dull-greyish colour, and the polysynthetic twin-lamellæ of the plagioclase are hardly distinguishable. Chloritic matter is also disseminated through some of the crystals. The nature of the plagioclase could, therefore, not be determined.

The most important and characteristic feature of this rock is the presence of the piedmontite as the secondary product. This is generally of large size, when found replocing the substance of the feldspar-phenocrysts, but in drusy cavities forms tufts of fine needles. In the former case, it does not take any regular form ; but commonly occurs as a granular aggregate, or in an imperfectly developed columnar shape, as shown in Fig. 2. A few quite perfect crystals were obtained by cautiously breaking the aggregate in a cavity with the edge of a knife.

Some of them are shown in Fig. 3. As usual, they are acicular in form, elongated in the direction of the *b*-axis. Basal cleavage is distinct, and some crystals are crossed by cracks transverse to the direction of elongation. Parallel growth of the individual crystals is not uncommon, and in consequence the surface of the crystals exhibits fine striations. The predominating faces are (001), (100), (101), (111). Besides, there are a few other faces, but so imperfectly developed that I could not measure them. Pleochroism is distinct, ranging between nearly colourless, light-yellow, and rosy-red. When the long side of the T (100) face coincides with the vibrating plane of the lower Nicol, it is nearly colourless (slightly orange-yellow in thick section), and when at right-angles it is light-rosy-red. M (001) face of the crystal is nearly colourless and light-lemon-yellow in the parallel and crossed positions respectively. Clinopinacoidal sections show lemon-yellow to rosy-red. The axial colours, thus determined are :

$\mathfrak{a}$=light-lemon-yellow,
$\mathfrak{b}$=colourless to light-orange-yellow,
$\mathfrak{c}$=rosy-red.

Absorption is $\mathfrak{c} > \mathfrak{a} > \mathfrak{b}$.

The colours in general are exceedingly feeble in intensity as compared

with those of the deep purple specimens from other localities, a difference due to the less amount of manganese present.

In convergent polarised light, the basal plane shows only one set of interference rings, inside fringed with red, outside with violet. The difference of dispersion of the two rays could not be measured because no plane containing the two poles was obtainable.

Common epidote also occurs in this rock, as I have mentioned before, and even in a crystal-aggregation the co-existence of the common and the manganese epidote is not rare. Fig. 4 shows an example of such a case. The mineral there figured was once feldspar, most probably, as may be conjectured from the outline of the pre-existing crystal, but no trace of the feldspar remains. Radiating needles of epidote, of characteristic olive-green colour, are at the right and left corners of the figure, and the light-rosy piedmontite in the centre. The transition from one to the other, however, is very gradual, showing how a small supply of manganese to the epidote has produced the piedmontite.

Both epidotes form a peculiar zonal stracture. The two minerals are alternately developed in the direction of the *b*-axis, as shown in Fig. 5, but not in concentric zones, so common in the glaucophane-schist of Otaki-san, described by B. Koto.* Basal section of these crystals shows, as seen from the figure, a beautiful rosy-red piedmontite zone in zigzag bands, parallel to the well-developed prismatic faces, and then succeeded by light-yellow common epidote in the direction of the *b*-axis. This fact indicates that these crystals have grown laterally, and that the zones with slightly but distinctly different chemical composition were formed layer by layer on the ends of the crystals.

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* B. Kotô, *op. cit.*

Occurrences of piedmontite as the secondary constituent of eruptive rocks have been noticed by only few petrographers.* Recently, this mineral was specially mentioned by late G. H. Williams as a component of the ancient rhyolite of the South Mountain.† The mode of occurrence and the mineralogical properties of it are nearly the same as those of the Shinano specimen. The only difference between them is in their colour. The piedmontite of the South Mountain rhyolite is of a deep colour, as usual, while the colour of this rhyolite is light.

I have to express my warmest thanks to Prof. B. Koto for the valuable advice which he has given me during this work.

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* Th. Liebisch found it in the red porphyrite of Egypt. Zeitschr., d. d. geol. Ges., vol. XXIX, p. 717, 1877. E. Haworth mentioned its presence in a porphyrite of Missouri, American Geologist, vol. I, p. 365, 1888. See also Johns Hopkins Univ. Circ., April number, 1883. J. P. Iddings noted its occurrence in the augite border around quartz-grains in a basalt from Nevada. *Geology of the Fureka District, Nevada*, Appendix B, p. 393.

† G. H. Williams, *Piedmontite and Scheelite from the ancient rhyolite of South Mountain Pennsylvania.* Am. Jour. Sci., vol. XLVI, p. 50, 1893.

PLATE VI.

Explanation of Plate.

Fig. 1. Geological Map of the environs of Ueda.

Fig. 2. ×38. A slide of piedmontite-rhyolite, showing the formation of piedmontite as a secondary product in the feldspar-phenocrysts. The feldspar-crysts also kaolinised. Porphyritic quartz showing many inlets of the ground-mass.

Fig. 3. Piedmontite needles. obtained by pulverising crystal aggregates in drusy cavities. Greatly magnified.

Fig. 4. Intergrowth of common epidote with piedmontite within a space formerly occupied most probably by a porphyritic crystal of feldspar. Greatly magnified.

Fig. 5. Piedmontite and epidote in zonal arrangement, developed in a lateral direction.

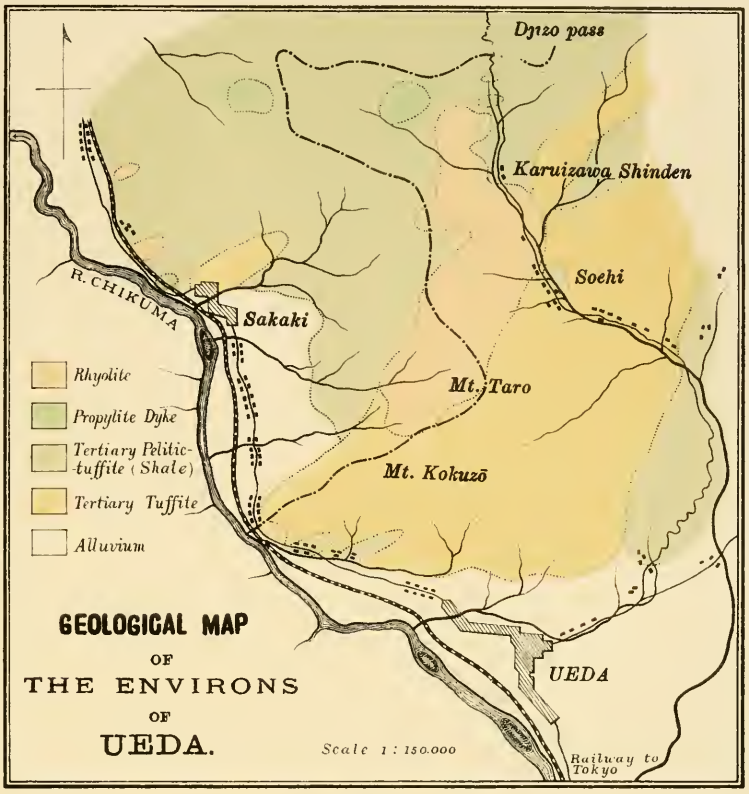

Fig. 1.

Fig. 2.

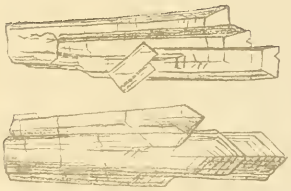

Fig. 3.

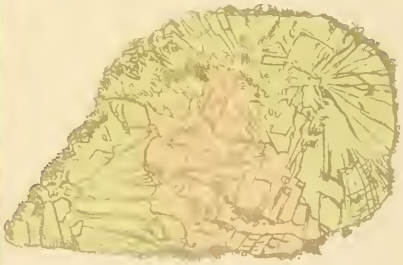

Fig. 4.

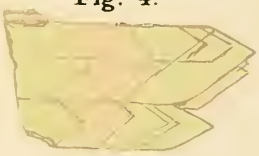

Fig. 5.

N. Yamasaki, Del.

The Atomic Weight of Japanese Tellurium.

By

Masumi Chikashige, *Rigakushi*,

College of Science, Imperial University.

The atomic weight of tellurium has been determined by Berzelius (1833), von Hauer (1857), Wills (1879), Brauner (1883 ; 1889), and Staudenmaier (1895). Berzelius gave it as 128·3 (O=16). Staudenmaier has only reduced it to 127·6. Brauner had also obtained this number, that is, 127·64, by determining the quantity of bromine in the tetrabromide ; but in other ways, which he could not admit to be naccurate, he obtained widely varying numbers for the atomic weight. To explain these variations, he assumed that what passes for the element tellurium is a mixture or compound. The number, 125, which since 1884 has been generally accepted as the atomic weight of tellurium, was suggested by Mendeléeff, but was adopted on the grounds of Brauner's determinations (partly by faulty methods, as he has since ascertained) published in 1883 in Russia. A paper by him, on the atomic weight of tellurium, which appeared last year in the *Journal of the* (London) *Chemical Society*, supplies no new data. It throws no light upon the causes of the varying results he had previously obtained by different methods, but apparently contains the admission from him at last that, so far as can be determined by known methods, the atomic weight of tellurium is 127·64 (127·7 *in vacuo*).

The object of the research described in the present communication to this Journal has been, not to add one more to the above

mentioned determinations of the atomic weight of tellurium, by some modification of a method already employed or by some new method, but to apply Brauner's tetrabromide method to tellurium of utterly different origin from that of what he worked upon. European and American tellurium occurs in association with heavy metals and might, therefore, when separated from those which are known, still retain unknown elements, in accordance with Brauner's conception. But in Japan tellurium is found in native sulphur, as was discovered by Divers, Shimose, and Shimidzu, in 1883 (*Chem. News ; J. Chem. Soc.*). There occurs, in fact, in this country a massive, crystalline, red sulphur, a variety of the *selensulphur* (Stromeyer) found in the Lipari Isles, in Naples (Phipson), and in the Hawaian Islands (Dana). It is semi-transparent and indistinguishable in appearance from native sulphur, except by its beautiful orange colour, and occurs interspersed with simple sulphur in the same blocks. I take from the *Chemical News*, the composition of a sample analysed by Divers and Shimidzu : —tellurium, 0·17 ; selenium, 0·06 ; arsenic, 0·01 per cent., traces only of molybdenum and earthy matter, and sulphur, by difference, 99·75 per cent. It is, accordingly much more a tellurosulphur than a selenosulphur.

Concerning this tellurium, it need not be contended that it is more truely an element than that found combined with bismuth, gold, lead, and silver ; it is sufficient to assert the high improbability that it should contain the same unknown elements as the latter. That being the case, then if it gives the same result by Brauner's tetrabromide method, as that obtained with Hungarian tellurium, the likelihood that tellurium with atomic weight 127·6 is an element is greatly increased, if not raised to a certainty. Such was the view taken of the matter by my honoured teacher, Dr. Edward Divers, F.R.S., who placed in my hands about 14 grams of tellurium, which

had been prepared by him and Mr. Shimose years ago. They had obtained this tellurium from the sediment removed from the lead-chambers of a sulphuric-acid factory, by a method the particulars of which they communicated to the *Chemical News* in 1883. The tellurium, which I thus received, had already been carefully freed from selenium and distilled in hydrogen.

Before I had made very much progress in preparing for the determination of the atomic weight, a preparation which has taken a very long time, Staudenmaier's memoir came to hand, but its contents did not deter me from finishing my investigation, though they can leave no reasonable doubt, I think, that the atomic weight of the element is really 127·6.

Long as the work has occupied me, there is now no occasion to describe it in detail, since it was purposely the closest copy I could make of Brauner's operations, so far as these seemed to be material to the point. The tellurium, already so pure, was tested for impurities, and was again distilled in hydrogen.

Excellent commercial bromine was distilled from potassium bromide, zinc oxide, and water (Stas). It was dehydrated first by means of anhydrous calcium bromide left in it for some days, and then by baryta, from which it was filtered through asbestus in vessels closed from the air. It was then distilled into a receiver sealed on to the distilling flask.

The silver was first precipitated by Stas's well-known sulphite method, fused under borax and nitre, then kept for a time in fusing potassium-sodium carbonate, washed with water, hydrochloric acid, and ammonia, melted again in a lime crucible, and granulated in distilled water.

The distilled water of the laboratory was fractionally redistilled, and the nitric acid was treated in the same way.

The balance used is one by Sartorius (his 1st quality), which has been hitherto only sparingly used for special cases. The weights are of quartz and platinum, from Gerhardt, and were found by me to have been closely adjusted.

The tellurium bromide was prepared by adding the tellurium to the bromine, in a tube, exactly as described by Brauner. In such a tube, he directly sublimed it, but I had to transfer it to another longer tube. The procedure was to slide into this tube nearly to the bottom an open tube loosely fitting it, down this to drop the powdery crude tetrabromide, and then withdraw it, leaving the walls of the sublimation tube unsoiled. This tube, at once closed by a cork, was then contracted about 25 cm. from its closed end and again about 12 cm. further off, where it was cut off from the corked end, and the narrowed mouth attached by caoutchouc tubing to the drying tube connected with a Sprengel pump. The tube was placed in the furnace with its first contraction just outside ; the bromide before sublimation occupied the hinder third of the tube within the furnace. Sublimation was in all other respects effected just as described by Brauner, a little dibromide being sublimed off at 200° into the outer part of the tube, and the tetrabromide sublimed at a temperature kept closely at 300° into the anterior part of the tube within the furnace. Practically nothing remained unsublimed, which showed that the transference of the undistilled bromide from tube to tube had been effected with impunity, this compound not being noticeably hygroscopic, and the air, at the time, being cold and very dry. The sublimation furnace was an exact copy of Brauner's.

The tellurium bromide was weighed off and dissolved in tartaric acid in one vessel, added to the silver nitrate, shaken for hours in the bottle, with a conical, polished, pointed, stopper projecting into it, and then finished off volumetrically, all just as described by Brauner

(except that the final titration was not effected in a dark room, but in feeble day light).

I made only the three determinations here given, neglecting a trial for practice, with good result, in which high accuracy was not sought for. The following are the results :—

Expt.	Tellm. brom.	Silver.	At. wt.
I.	4·1812	4·0348	127·57
II.	4·3059	4·1547	127·61
III.	4·5929	4·4319	127·58

The details of Exp. II. are :—Silver weighed off, 4·1548 grams ; time of continuous shaking by water-motor, 4 hours ; precipitate, thoroughly pulverulent ; silver solution added, 0·4 cc., which produced no turbidity ; potassium bromide solution required, 0·8 cc.= 0·54 cc. silver solution. Since there had been taken silver in excess, equivalent to 0·14 cc. silver solution, and, therefore, 0·00014 grams silver, the actual quantity of silver required by the 4·3059 grams bromide had been 4·1547 grams. Then :—

$$\frac{79{\cdot}963 \times 4{\cdot}1547 \times 100}{107{\cdot}938 \times 4{\cdot}3059} = 71{\cdot}48\% \text{ bromine}$$

and—

$$4\left(\frac{107{\cdot}938 \times 4{\cdot}3059}{4{\cdot}1547} - 79{\cdot}963\right) = 127{\cdot}61 \text{ at. wt. tellurium.}$$

In Exp. I., the silver weighed out was not so closely apportioned, and several cubic centimeters of the volumetric solution had to be used ; otherwise, it agreed with II., as did also III. in its details.

When it is considered that Brauner and I have obtained by the same method identical results, although he worked with tellurium that had presented itself in combination with metals, while I have worked with that occurring in native sulphur of high purity, except

for the presence of this tellurium and of selenium, so far as can be ascertained by tests for known elements, and when it is further considered that Staudenmaier's results are the same as Brauner's, though obtained by a wholly different method, no reasonable doubt can remain that the atomic weight of tellurium is 127·6.

The occurrence of tellurium in Japan in association with selenium in native sulphur is also a fact of great significance in settling the place of this substance in a natural classification of the elements, showing, as this does, so close a habitude to exist between it and sulphur and selenium.

Das Johanniskäfer-Licht.

Von

H. Muraoka. *Rigakuhakushi. Dr. Ph.*

Prof. der Physik am Dai-San Kōtōgakkō.

Die Entdeckung von H. Becquerel,* dass gewisse fluorescirende Körper, wie Uraniumsalze, Strahlen aussenden, welche ähnliche Eigenschaften besitzen, wie die Röntgen' schen, führte mich zu der Vermuthung, dass auch Johanniskäfer's Licht, dessen aüsseres Aussehen doch sehr an Fluorescenz erinnert, ebenfalls ein solches Verhalten zeigen könnte. Im Folgenden theile ich meine daraufbezügliche Untersuchungen mit, bemerke aber, dass während der Arbeit die Johannis-Jahreszeit allmälig ihrem Ende sich nahte, so dass viele wichtige Probleme nur flüchtig berührt werden mussten. Die Versuchen konnten daher nicht systematisch genug und auch nicht oft genug wiederholt werden, um Schlüsse mit Sicherheit daraus zu ziehen. Doch möchte ich betonen, dass bei der Behandelung der photographischen Platten Einflüsse des Sonnen-oder Lampen-Lichtes stets mit Sorgfalt vermieden worden sind.

Bei dem ersten Versuche legte ich Kupfer-, Aluminium-, Zink- und Messing- Platten von gleicher Grösse auf eine photographische Trockenplatte nebeneinander (Versuch I). Um jedoch die letztere von der direkten Berührung mit den harten Metallen zu schutzen, war jede Metallplatte mit einer Kartonunterlage versehen, welche in der Mitte einen kreisförmigen Ausschnitt hatte. Das ganze wurde mit

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* H. Becquerel, C. R. 122. p. 420, 501-503, 559-564, 689-694, 762-767. 1896.

schwarzem Papier 3-4 mal umwickelt, und auf den Boden eines flachen Kistchens hineingelegt. Darin wurden etwa 300 Johanniskäfer hineingethan, deren Wegfliegen mit einem Hanfnetz verhindert wurde. Diese Operation wurde in einem guten photographischen Zimmer vorgenommen und das Ganze zwei Nächte stehen gelassen.

Der Zweck dieses Experimentes war zu sehen, ob erstens die durch schwarze Papierschichten filtrirten Käfer-Strahlen überhaupt fähig seien durch die Metalle hindurchzugehen und noch auf die photographische Platte zu wirken. Zweitens erwartete ich, dass wenn dieses der Fall sein sollte, durch die Stärke der Schwärzungen der Ausschnittsstellen von Kartonunterlagen, den Grad der Durchlässigkeiten eventuell schätzen zu können. Als nun die Platte entwickelt wurde, sah ich etwas ganz auffallendes. Nicht die ausgeschnittenen Stellen der Kartonunterlagen, sondern die Stellen, wo dieselben die photographische Platte berührten, waren stark angegriffen, d. h. ganz geschwärzt, während die Ausschnittsstellen alle gleich hell geblieben sind.

Die Richtung der Untersuchung wurde hierdurch auf diese Erscheinung abgelenkt, und da von derselben noch vielfach gesprochen werden soll, so bezeichne ich sie kurz mit dem Worte " Saugphänomen " aus einem Grunde, welcher bald angegeben werden soll. Dieses Resultat erinnerte mich an die Arbeit von John Macintyre,* welcher bei seinen Versuchen über Photographien durch undurchlässige Substanzen ohne Crookes' Röhre, die Ansicht ausspricht, dass Contactwirkung gewisse Rolle spielen könnte. Die Contactwirkung kann nun darin bestehen, dass die Berührung des Kartons und der Metalle elektrische Potentialdifferenz verursacht, welche dann unter dem Einflusse der filtrirten Käfer-Strahlen photographisch wirksam wird. Um das zu prüfen, schichtete ich Kupfer über Zink und Zink über Kupfer, verfertigte ferner zwei Zamboni'sche Säulen von 15 Platten-

* J. Macintyre. Nature 20. Febr. p. 379. 1896.

paaren, und legte dieselben auf eine photographische Platte (Versuch II.). Diese wurde dann genau so behandelt wie bei dem vorhergehenden Versuche. Das Resultat war, dass sowohl Cu/Zu— und Zu/Cu— Platten, als auch die beiden Zambonischen Säulen mehr oder weniger durchlässig sind, dass aber die Schwärzungen bei weitem nicht so intensiv waren, wie bei dem Saugphänomen. Darnach scheint die Contactelectricität nicht die Ursache des Saugphänomens zu sein.

Um zu sehen ob blosse Berührung des Kartons mit der photographischen Platte selbst die Ursache sei, stellte ich den Versuch I ohne Metallbedeckung an, so dass eine Kartonscheibe mit Ausschnitt allein auf die photographische Platte zu liegen kam (Versuch III). Hierbei zeigte sich die Ausschnittsstelle ganz schwarz und die Berührungsstelle nur wenig angegriffen, also genau umgekehrt wie bei dem Versuche I. Es kann also eine blosse Berührung des Kartons mit der photographischen Platte auch nicht der Grund des Saugphänomens sein.

Zur weiteren Prüfung führte ich den Versuch I umgekehrt aus, indem dieses mal die Metallplatten direkt an die photographische Platte und darauf die Kartonscheiben mit Ausschnitten gelegt wurden (Versuch IV). Die Entwickelung zeigte leichte gleichförmige Schwärzungen ohne die Ausschnittsstellen zu markiren. Ferner trat das Saugphänomen nicht ein, wenn über Kupferplatte mit Ausschnitt eine Kartonscheibe ohne Ausschnitt (oder eine Kupferplatte ohne Ausschnitt) aufgelegt (Versuch V) und genau so behandet wurde, wie bei dem Versuche I.

Es scheint also für den Eintritt des Saugphänomens nothwendig zu sein, dass die Kartonscheibe mit Ausschnitt direkt auf die photographische Platte zu liegen kommt und darauf eine Karton-oder Metallplatte gelegt wird, welche die durch mehrere Schichten von schwarzem Papier filtrirten Käferstrahlen noch einmal filtrirt. Auch schenit eine Schichtung (Versuch VI) von mehreren Kartonscheiben mit

Ausschnitten (die Ausschnittsstellen über einander) das Saugphänomen zu verstärken, d. h. den photographischen Angriff zu befördern.

Diese Erscheinung macht wir den Eindruck von derjenigen der Permeabilität des Eisens für magnetische Kraftlinien. Vielleicht ist das Kartonpapier für Strahlen, welche durch Filtration durch Papierschichten erhalten worden sind (vergl. Versuch III), weniger und für die nocheinmal durch Metalle oder Karton filtrirten Strahlen (vergl. Versuch I) mehr permeable. Dies ist der Grund, weshalb ich diese Erscheinung " Saugphänomen " nannte. Da jedoch keine greifbare Erklärung dafür gefunden werden kann, so soll dieses Wort Nichts behaupten, sondern bloss als eine abkürzende Bezeichnung gebraucht werden. Ob eine Metallplatte mit Kartonunterlage ohne Ausschnitt auch eine ebenso starke Schwärzung verursacht, das habe ich leider ausgelassen zu untersuchen.

Was nun die Durchlässigkeit anbetrifft, so zeigten 3 Metallen folgende Reihenfolge :

Al, Cu, Sn.

Die Dicke scheint merkwürdiger Weise keine wichtige Rolle zu spielen, wie es auch J. Macintyre[1] mit seinem Tesla-Transformator gafunden hat. Glas ist durchlässig und zwar ohne Differenz von Färbungen, welches Resultat an den Noden'schen Versuch[2] mit Röntgen-Strahlen erinnert. Turmalin, Kalkspath sind durchlässig. Auch Fluorescin—, Uraniumacetat-Pulver sind durchlässig, während Y. Yamaguchi und T. Mizuno,[3] K. Yamagawa[4] und H. Becquerel[5] gefunden haben, dass fluorescenz-erregende Substanzen für Röntgen-Strahlen undurchlässig sind. Holz ist mehr durchlässig als Metalle und

1) J. Macintyre, Nature l. c.
2) Noden, C. R. 122. p. 237. 1896.
3) Y. Yamaguchi und T. Mizuno, Rentogen Tōyei Shashinchō p. 17. 1896.
4) K. Yamagawa, Tokyo Butsurigakko Zassi Nr. 55. p. 202. 1896.
5) H. Becquerel, C. R. l. c.

zwar lassen die weicheren Stellen mehr Strahlen hindurch als die Fasern. Es zeigen also die durch Papierschichten filtrirten Strahlen gewisse Abhängigkeit zwischen den Durchlässigkeiten und den specifischen Gewichten, wie die Röntgen-Strahlen. Auch werfen die Käfer-Strahlen deutliche Halbschatten in den Photographien, wie die Röntgen-Strahlen.

Im Verlaufe der Versuche wurde ich immer mehr gewahr, dass die Eigenschaften der Käfer-Strahlen wesentlich von den filtrirenden Substanzen abhängen müssen. Daher stellte ich eine Reihe von Versuchen auf, mit unfiltrirten, mit durch Karton oder Kupfer filtrirten Käferstrahlen, deren Ergebnisse noch mitgetheilt werden sollen.

Es ergaben sich, dass unfiltrirte Käferstrahlen sich verhalten ganz wie gewöhnliche Lichtstrahlen. So z. B. zeigte die Platte, wolche wie bei dem Versuche I preparirt war, unter den Metallplatten keine photographische Wirkung, so dass auch keine Spuren von Ausschnitten der Kartonunterlagen zu bemerken war. Substanzen, die dem gewöhnlichen Lichte undurchlässig sind, erwiesen sich auch den unfiltrirten Strahlen undurchlässig. Ferner konnte Reflection, Refraction und Polarisation leicht nachgewiesen werden.

Filtrirt man aber das Käferlicht durch dickes (etwa 3^{mm}) Kartonpapier, so erhält man im Allgemeinen dieselben Resultate wie bei der Filtration durch Schichten von schwarzem Papier. Abweichend war doch das Resultat, dass das Saugphänomen erhalten wurde, auch ohne Bedeckung. Auch Ebonit ohne Bedeckung zeigte dieselbe Erscheinung. Holzphotographie zeigte auch die Fasern wie vorher.

Bei der Kupfer-Filtration tritt kein Saugphänomen ein. Auch konnte eine Schichtung von Kartonscheiben (vergl. Versuch VI) das Saugphänomen nicht zu Stande bringen. Auffallend ist die Photographie von der Holzplatte ; die Stellen der Fasern sind mehr angegriffen als die weicheren Stellen, also gerade umgekehrt wie bei den Filtrationen

durch Papierschichten oder durch Karton. Dieses Resultat erinnerte mich an die Resultate von John Macintyre* welcher gefunden hat, dass man durch Tesla-Transformator jenach der Behandelungsweise positive oder negative Photographien erhalten kann. Wenn auch J. Macintyre's und meine Resultate aüsserlich sehr ähnlich aussehen, so sind die Gründe ganz verschieden. Denn, bei den Holzphotographien liegt der Unterschied in den filtrirenden Substanzen. Um dennoch zu sehen, ob die J. Macintyre's Behandelungsweise auch bei den Holzplatten mit filtrirten Käferstrahlen Einfluss hätte, wiederholte ich den Holzplatten-Versuch noch einmal, mit dem Unterschiede uur, dass eine Kupferplatte hinter die photographische Platte gelegt wurde, wie J. Macintyre es gethan hat. Das Resultat wurde aber dadurch nicht geändert. Ferner habe ich seinen Versuch, den er unter dem Rath von Lord Kelvin ausgeführt hat, wiederholt, indem ich eine auf eine photographische Platte gelegte Holzplatte in eine Kupfer-Kiste lichtdicht verschloss und die letztere gut zur Erde ableitete. Dies wurde der Einwirkung von etwa 300 Käfern ausgesetzt. Während J. Macintyre keine photographische Einwirkung nachweisen konnte, erhielt ich ein wohlgeprägtes Bild wie vorher. Nach diesen Versuchen müssen die durch Kupfer filtrirten Käferstrahlen von ganz anderer Natur sein, wie Strahlen, welche ein Tesla-Transformator aussendet.

Sowohl bei der Karton—, als auch bei der Kupfer-Filtration habe ich eine Reihe von Versuchen über Durchlässigkeiten ausgeführt, indem ich Kupfer als zu vergleichenden Gegenstand auswählte. Auf jede photographische Platte wurden gewöhnlich vier zu untersuchenden Gegenständen gelegt, deren eine die Normalkupferplatte war. Vier bis sechs von so preparirten Platten wurden in eine grössere flache Holzkiste hineingethan, worauf in einer Entferung von etwa 5^{mm} die filtrirende Platte zu liegen kam. Als Lichtquelle dienten etwa

* J. Macintyre, Nature l. c.

1000 oder mehr Käfer. Es wurde vorsichtig dafür besorgt, dass kein direktes Licht hineingehen kann. Die Expositionszeit betrug 2-3 Tage. Nach der Entwickelung sah man gewöhnlich, dass die Normalkupferplatten nicht alle gleichdunkel sind. Dies muss gewiss von der ungleichmässigen Vertheilung der Käfer herrühren, was an den unsymetrischen Stellungen von Halbschatten dicker Gegenständen zu erkennen ist. Es ist also nicht leicht eine exacte Skala der Durchlässigkeit herzustellen, so lange man kein Mittel hat, die Käfer an bestimmten Stellen zu fesselen. Da ausserdem viele Photographien misslungen sind, so kann ich über die Durchlässigkeit der durch Karton und durch Kurpfer filtrirten Strahlen gemeinschaftlich nur folgendes mittheilen: Topas, Kalkspath, Salpeter, Feldspath (3^{mm} dick), Gumi, Tuch, Seide, Medizinische Capsel (hatte den Zweck nachher Flüssigkeiten zu untersuchen) sind mehr oder weniger durchlässig. Achat zeigte deutlich die darin enthaltene Skeletkrystall (Eisensilicat ?). Ei-Schale ist undurchlässig. Aluminium und Kupfer scheinen jenach der Filtration ihre Durchlässigkeiten zu ändern in ähnlicher Weise wie die weichen und dichteren Stellen von Holz. Recht curios war die Photographie von Quarz. Derselbe war nämlich eine senkrecht zur Axe geschnittene Platte, deren Seite ganz glatt cylinderisch abgeschliffen war. In der Photographie desselben trat eine caustische Curve sehr deutlich auf. Es muss bei diesem Versuche die Käfer sich mehr an eine bestimmte Seite hingestellt haben. Hiernach ist die regelmässige Reflection sicher vorhanden. Karton-Filtration scheint Strahlen zu liefern, welche mittlere Eigenschaften haben, wie Papierschichten- und Kupfer-Filtrationen. Ebonit-Filtration, welche ich wegen Mangel an Käfern noch viel roher ausführen konnte, scheint auch ein Mittelding zwischen Karton- und Kupfer-Filtrationen zu sein. Darnach könnte vielleicht die Dichtigkeiten der filtrirenden Substanzen die Eigenschaften der Strahlen bedingen.

Interferenz und Polarisation konnte ich leider nicht nachweisen, doch bin ich überzeugt, dass sie vorhanden sind.

Versuche über die Einwirkung auf Radiometer und dynamische Entladung der Elektricität gaben negative Resultate.

Die Thatsache, dass unfiltrirte Käferstrahlen sich wie gewöhnliches Licht verhalten, also für Metalle z. B. undurchlässig sind, während die filtrirten Strahlen durch Metalle sogar durch Feldspath von 3^{mm} Dicke hindurchgehen, deutet hin, dass solche Strahlen erst bei der Filtration erzeugt werden. Analog könnte es auch mit der Quelle der Röntgen-Strahlen sein. Dieselbe wird weder an der Kathode noch an der Anode zu suchen sein, sondern die Filtration der Kathoden—oder vielleicht der Anoden—Strahlen durch Glaswand wird erst Strahlen gewisser Art erzeugen, und wenn die so erhaltenen Strahlen noch weiter durch Holz, Pappe, Aluminium etc. filtrirt werden, so werden wohl Strahlen von immer anderer Natur, möglicherweise homogener erhalten. Wäre dies wirklich der Fall, so würde man in der Filtration eine Methode der Homogenisirung der Röntgen-Strahlen finden. Und wenn dieselben homogen genug erhalten worden sind, so wäre es nicht unmöglich Reflection, Interferenz und Polarisation noch deutlicher nachzuweisen als bis jetzt. Die filtrirten Käfer-Strahlen sind mehr den Becquerel'schen Fluorescenz-Strahlen ähnlich als den Röntgen'schen, so dass sie auch wahrscheinlich ein Mittelding zwischen ultravioleten und Röntgen-Strahlen bilden. Somit bin ich geneigt aus der Analogie mit J. J. Thomson* zu schliessen, dass Röntgen-Strahlen transversal sind.

Uebersicht.

Die Resultate lassen sich kurz zusammenfassen wie folgt :

1. Das natürliche Käferlicht verhält sich wie das gewöhnliche

* J. J. Thomson, Nature 23. April p. 581. 1896.

Licht.

2. Die durch Filtration des natürlichen Käferlichtes durch Karton oder durch Kupferplatte etc. erhaltenen Strahlen haben ähnliche Eigenschaften wie die Röntgen'schen oder die Becquerel'schen Fluorescenz-Strahlen.

3. Die filtrirten Käferstrahlen zeigen dem Karton gegenüber ein auffallendes Verhalten, das Saugphänomen, welches dem Verhalten der magnetischen Kraftlinien gegen Eisen ähnlich ist.

4. Die Eigenschaften der filtrirten Käferstrahlen scheinen von den filtrirenden Substanzen abzuhängen, vielleicht von der Dichtigkeit der letzteren.

5. Es scheint, dass die unter 2. angegebenen Eigenschaften erst bei der Filtration erzeugt zu werden. Analog könnten x-Strahlen auch erst bei der Filtration erzeugt werden und die Filtration mag ein Mittel geben, x-Strahlen zu homogenisiren.

6. Die filtrirten Käferstrahlen zeigen deutliche Reflektion. Refraktion, Interferenz und Polarisation konnten nicht nachgewiesen werden, doch glaubt der Verfasser, dass sie vonhanden sein werden.

7. Die filtrirten Käferstrahlen scheinen wie die Becqurel'schen Fluorescenz-Strahlen mittlere Eiginschaften zwischen ultravioleten und Röntgen-Strahlen zu besitzen, so dass sie der J. J. Thomson'schen Schlussweise über die Tranversalität der Röntgen-Strahlen einen Beitrag liefern.

Johanniskäfer.

Es wird nicht uninteressant sein, etwas vom Käfer selbst zu besprechen. Die Käfer, welche am Anfang dieser Arbeit gebraucht wurden, waren recht gross. Der grösste 20^{mm} lang, im Mittel etwa 13^{mm}—15^{mm}. Gegen Ende konnten nur sehr kleine erhalten werden, von etwa 8^{mm} Länge. Fin grosser Käfer hat 2 Reihen von leuchten-

den Kügelchen am Unterleib, während ein kleiner 3 Reihen besitzt, also verhältnissmässig viel Licht aussendet. Photographisch wirksam ist aber nicht nur dieser leuchtende Theil, sondern fast der ganze Körper. Als nämlich in dem photographischen Zimmer ein Käfer zufällig auf eine empfindliche Platte angeflogen kam, entwickelte ich sie sofort und erhielt eine netzartige Abbildung des ganzen Käfers, jedoch war die Stelle des Unterleibes stärker angegriffen. Da die photographisch wirksame Strahlen wahrscheinlich durch die Flügeln mit Leichtigkeit hindurchgehen (oder vielleicht erst beim Durchgang durch Flügeln erzeugt werden), so wird es zum Photographiren, abgesehen von der Entfernung, ziemlich gleichgültig sein, ob die Käfer ihre vordere Seiten oder Rücken der photographischen Platte zukehren. Die Käfer leuchten von etwa 6 Uhr Abends bis 11 Uhr Nachts am stärksten. Um die Käfer möglichst lang lebend zu erhalten, muss man sie zwischen den Experimenten, also wo sie nicht gebraucht werden, mit Wasser bespritzen. Zuckerwasser ist nutzlos, wenn auch man viel davon spricht. Verstärkung des Leuchtens mit Sauerstoff ist erfolglos. Todte Käfer leuchten noch, solange sie sich nicht ganz vertrocknen, besonders wenn man sie abreibt. Johanniskäfer gehört zu einer der Sehenswürdigkeiten der Stadt Kyōto, wo diese Arbeit gemacht worden ist. Etwa Mitte Juni sieht man bei Nacht tausende von Käfern die malerische Umgebung der Stadt beleuchten. Doch dauert die Jahreszeit nicht lang genug, um eingehendere Studien zu machen und es wird mir sehr lieb sein, wenn jemand die Güte haben wollte, Methode des Käferzuchtes mitzutheilen.

In alten japanischen Büchern sollen geschrieben stehen, dass man Bambusrohr erweichen kann, indem man es mit Johanniskäfer kocht.

Es wird interessent sein, auch andere leuchtende Dinge, wie Infusorien, Seezungen, verwesende Substanzen etc. zu untersuchen.

Endlich muss ich Herrn M. Kasuya meinen Dank aussprechen, dass er mit der Lieferung von Käfern, der Entwickelung der photographischen Platten etc. so eifrig mich beholfen hat.

Nachtrag.

Während des Druckes war Herr K. Yamagawa so freundlich mich darauf aufmerksam zu machen, dass ich bei der Beobachtung des natürlichen Käferlichtes mich getäuscht haben könnte. Er meint, dass wenn die photographische Wirkung gleich derjenigen des gewöhnlichen Lichtes erscheint, so könnte doch derjenige Theil, welcher unangegeriffen aussieht, in der Wirklichkeit angegriffen sein, was nur wegen Contrast neben sehr schwarzen Stellen weissen Eindruck macht. Nach dieser Bemerkung habe ich nachträglich die photographischen Bilder verglichen und finde, dass Herr K. Yamagawa möglicher Weise recht haben kann. Um aber diesen Punkt mit Sicherheit zu entscheiden, müssen die Versuche speciell für diesen Zweck nachgeholt werden, und ich gedenke dieselben sowohl, als auch viele andere im nächsten Jahre noch einmal und zwar etwas systematischer auszuführen.

Physikalisches Institut des Dai-San Kōtōgakkō. Kyōto, Japan.

On the Prediction of Solar Eclipses.

By

Shin Hirayama, *Rigakushi,*

Professor of Astronomy, Science College, Imperial University, Tōkyō.

1. *Introduction.* For the prediction of eclipses several methods of computation have been proposed by different authors. Among them the methods of Bessel, Hansen, and Woolhouse are used by different nations for the construction of their ephemerides. Besides these, there is another method given in Sawitsch's "*Abriss der praktischen Astronomie*, 1879," which is said to have been invented by Gauss. As described by Zech, it is similar to Hansen's method. Hence, for the delineation of the curve the time is not always taken as the argument, as in the case of rising and setting limits. In the following pages I have treated this system of co-ordinates as Bessel has treated his. The way of discussion is quite similar to that in Chauvenet. In many cases it would be sufficient only to substitute for x, y, etc., of Bessel the corresponding quantities in the other system of co-ordinates. But I have thought it better to develop the complete formulæ for convenience of computation. I have also given the approximate formulæ for the computation of the northern and southern limits of the umbra.

2. *Fundamental equations of Eclipses.* The line joining the centres of the sun and the earth is taken as the axis of z, positive towards the sun. Let the plane passing through the centre of the moon and perpendicular to the axis of z be the plane of reference, the

point of intersection of this plane and the axis of z being the origin. The axis of y is the intersection of the plane of reference and the declination plane of the sun, positive towards the north pole. The axis of x is perpendicular to the y axis in that plane of reference and is positive towards the point whose right ascension is greater by 90° than that of the sun.

Referred to this system of co-ordinates, let us assume—

x, y, 0 = the co-ordinates of the moon ;

ξ, η, 0 = the co-ordinates of the point of intersection of the line joining the observer and the sun with the plane of reference ;

D = the distance of this point from the moon ;

α, δ = the geocentric right ascension and the declination of the moon, respectively ;

α', δ' = the geocentric right ascension and the declination of the sun, respectively ;

π, π' = the equatorial horizontal parallax of the moon and the sun, respectively ;

r, r' = the geocentric semidiameter of the moon and the sun, respectively ;

z', v = the geocentric zenith distance and the parallactic angle of the sun, respectively ;

φ, φ' = the geographical and the geocentric latitude, respectively ;

ρ = the radius of the terrestrial spheroid for the latitude φ ;

t = the hour angle of the sun ;

e = the equation of time.

Then, we have the following formulæ, the derivation of which, being explained in the work of Sawitsch, is here omitted.

The distance between the moon and the centre of the earth is taken as the unit of distance.

$$\left.\begin{aligned} x &= \cos\delta \sin(\alpha-\alpha') \\ y &= \sin\delta \cos\delta' - \cos\delta \cos\delta' \cos(\alpha-\alpha') \end{aligned}\right\} \quad \ldots\ldots(1)$$

$$\Pi = (\pi-\pi') \sqrt[3]{\cos(\pi-\pi')} \quad \ldots\ldots(2)$$

$$\left.\begin{aligned} \xi &= \Pi\rho \cos\varphi' \sin t &&= \Pi\rho \sin z' \sin v \\ \eta &= \Pi\rho \sin\varphi' \cos\delta' - \Pi\rho \cos\varphi' \sin\delta' \cos t &&= \Pi\rho \sin z' \cos v \\ &\quad \sin\varphi' \sin\delta' + \cos\varphi' \cos\delta' \cos t &&= \cos z' \end{aligned}\right\} \quad \ldots\ldots(3)$$

$$\left.\begin{aligned} D \sin\sigma &= (x-\xi) \\ D \cos\sigma &= (y-\eta) \end{aligned}\right\} \quad \ldots\ldots(4)$$

where

$$\left.\begin{aligned} D &= r + r'(1-\rho \sin\pi \cos z') \text{ for the partial eclipse} \\ D &= r - r'(1-\rho \sin\pi \cos z') \quad ,, \quad ,, \text{ total eclipse} \\ D &= r'(1-\rho \sin z \cos z') - r \quad ,, \quad ,, \text{ annular eclipse} \end{aligned}\right\} \quad \ldots\ldots(5)$$

and σ is the angle between the declination circle of the sun and the line joining the apparent places of the sun and the moon, and is reckoned positive towards the positive axis of x on the plane of projection.

For convenience in computation, the formulæ (1) may be put in the following form—

$$\left.\begin{aligned} x &= (\alpha-\alpha') \cos\delta \sqrt[3]{\cos(\alpha-\alpha')} \\ y &= (\delta-\delta') \sqrt[3]{\cos(\delta-\delta')} + \frac{1}{2} \sin 1'' \frac{\sin\delta'}{\cos\delta} x^2. \end{aligned}\right\} \quad \ldots\ldots(1)a$$

Eqns. (4) are the fundamental equations of the theory of eclipses.

3. *The outline of the shadow upon the earth at a given time.*

This outline is the curve on the surface of the earth, from every point of which a contact of the sun's and moon's limits may be observed at the given time. Or, it is the intersection of the cone of the shadow with the earth's surface.

Let T_0 = the given time, reckoned at the first meridian and let

x, y, and Π be taken from the tables for the given time. Then the co-ordinates, ξ, η, of any place at which a contact may be observed at the given time, must satisfy the condition (4)

$$\left.\begin{array}{l} D \sin\sigma = x - \xi \\ D \cos\sigma = y - \eta \end{array}\right\} \text{ or } \left.\begin{array}{l} \xi = x - D \sin\sigma \\ \eta = y - D \cos\sigma. \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots(4)a$$

Let

t=the hour angle of the sun

L=the east longitude of the place

then we have

$$t = T_0 + L - e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Supposing σ to be an arbitrary variable, what we want is to find out φ and L from the equations (4), (3), (5) and (6).

First, let us solve the equations (3) for φ' and t.

Put

$$\left.\begin{array}{l} \rho \sin\varphi' = (1-c) \sin\varphi_1 \\ \rho \cos\varphi' = \qquad \cos\varphi_1 \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where

$$c = \frac{1}{299.15}.$$

Then,

$$\xi = \Pi \cos\varphi_1 \sin t;$$

$$\eta = \Pi (1-c) \sin\varphi_1 \cos\delta' - \Pi \cos\varphi_1 \sin\delta' \cos t.$$

Again, put

$$\left.\begin{array}{l} (1-c) \cos\delta' = l \cos\delta_1 \\ \sin\delta' = l \sin\delta_1 \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

then

$$\left.\begin{array}{l} \xi = \Pi \cos\varphi_1 \sin t \\ \eta = \Pi\, l\, [\sin\varphi_1 \cos\delta_1 - \cos\varphi_1 \sin\delta_1 \cos t] \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots(9)$$

Further, putting

$$\left.\begin{aligned} \sin B &= \frac{\xi}{\Pi} = \rho \sin z' \sin v \\ \cos B \sin A &= \frac{\eta}{\Pi\, l} = \frac{\rho}{l} \sin z' \cos v \\ \cos B \cos A &= \cos z' \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots(10)$$

we have now the required solution

$$\left.\begin{aligned} &\cos \varphi_1 \sin t = \sin B \\ &\cos \varphi_1 \cos t = \cos B \cos (A + \delta_1) \\ &\sin \varphi_1 \quad = \cos B \sin (A + \delta_1) \\ &\tan \varphi = \frac{\tan \varphi_1}{1-c} \quad L = t - T_0 + e \end{aligned}\right\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

where e is the equation of time.

4. *Visibility.*—In order that the eclipse may be visible from a point on the earth's surface, we must have z' less than 90° ; that is, $\cos z'$ must be positive, and therefore $\cos A$ and $\cos B$ must have the same sign. Let us choose $\cos B$ to be always positive, then $\cos A$ is also, necessarily, positive. In this way we can determine A and B without ambiguity.

For the first approximation, we must put (5) in the form

$$\left.\begin{aligned} D &= r + r' \quad \text{for the penumbra.} \\ D &= r - r' \quad \text{,, ,, umbra.} \end{aligned}\right\} \ldots\ldots\ldots\ldots\ldots\ldots(12)$$

This value of D and the assumed value of σ give ξ and η from (4)a. Having found ξ and η, the equation (10) and (11) will give the required value of φ and L.

The value of δ_1 and l in (8) may directly be taken from table II.

Table I gives the value of $\varphi - \varphi_1$, φ_1 being the argument.

This was kindly computed by Mr. Matsuzaki of Tōkyō astronomical Observatory.

5. *Criterion of beginning or ending of the eclipse.*

The negative or positive value relatively to the time of the differential co-efficient of the quantity D gives the criterion of beginning or ending of the eclipse.

$$\frac{dD}{dT} \sin\sigma + D \cos\sigma \frac{d\sigma}{dT} = x' - \xi' ;$$

$$\frac{dD}{dT} \cos\sigma - D \, sid\, \sigma \frac{d\sigma}{dT} = y' - \eta' ;$$

$$\frac{dD}{dT} = (x' - \xi') \sin\sigma + (y' - \eta') \cos\sigma .$$

Putting $\frac{dt}{dT} = k' = \frac{15}{57.296}$, $\log k' = \bar{1},41797$; we have

$$\xi' = k' \, \Pi\rho \cos\varphi' \cos t ; \qquad \eta' = k' \, \Pi\rho \cos\varphi' \sin\delta' \sin t .$$

Put $x' = n \sin N$; $\cos t = f \cos F$;

$y' = n \cos N$; $\sin\delta' \sin t = f \sin F$;

then, we have

$$\frac{dD}{dT} = n \cos(\sigma - N) - k' \, \Pi\rho . f . \cos\varphi' . \sin(\sigma + F).$$

Except in the case where $\sigma - N$ is nearly equal to 90°, the second term is far less than the first. Hence $\frac{dD}{dT}$ is negative or positive, that is, the eclipse is beginning or ending, according as

$$\sigma - N > 90^\circ \text{ but } < 270^\circ,$$

or

$$\sigma - N < 90^\circ \text{ but } > 270^\circ.$$

If $\sigma - N$ is nearly equal to 90°, then compute $\frac{dD}{dT}$ by the strict formulæ above given.

6. *To find the rising and setting limits of the eclipse.*

By these limits we mean the curves upon which are situated all those points of the earth's surface where the eclipse begins or ends with the sun in the horizon.

This gives $\sin z'=1$. Now, let it be required to find the place where this condition is satisfied at a given time. Since $\xi=\Pi\rho \sin v$, $\eta=\Pi\rho \cos v$, we have (4) transformed into the form

$$D \sin \sigma=x-\Pi\rho \sin v\,;$$

$$D \cos \sigma=y-\Pi\rho \cos v.$$

Let

$$\left.\begin{aligned} m \sin M&=x \\ m \cos M&=y \end{aligned}\right\} \quad\text{.....(12)}$$

then from the equations

$$D \sin \sigma=m \sin M-\Pi\rho \sin v\,;$$

$$D \cos \sigma=m \cos M-\Pi\rho \cos v\,;$$

we deduce, by adding their squares,

$$D^2=m^2-2m\,\Pi\rho \cos (M-v)+\Pi^2\rho^2\,;$$

$$2 \sin^2 \frac{M-v}{2}=1-\cos (M-v)=\frac{D^2-(m-\Pi\rho)^2}{2m\,\Pi\rho}\,.$$

If, then, we put $\lambda=M-v$, we have

$$\left.\begin{aligned} \sin \frac{1}{2}\lambda&=\pm\sqrt{\frac{(D+m-\Pi\rho)(D-m+\Pi\rho)}{4m\,\Pi\rho}} \\ v&=M\pm\lambda \end{aligned}\right\} \quad\text{.....(13)}$$

in which $\frac{1}{2}\lambda$ may always be taken to be less than 90°, but the double sign gives two points satisfying the given condition. For the first approximation, assume ρ to be equal to the radius corresponding to a mean latitude of 45°. With the value of v thus found, we have, for finding latitude and longitude of the required point, the formulæ—

$$\left.\begin{array}{l} \cos\varphi' \sin t = \sin v \\ \cos\varphi' \cos t = -\cos v \sin\delta' \\ \sin\varphi' \quad = \cos v \cos\delta' \\ L = t - T_0 + e \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

We may easily find the geographical latitude from the geocentric.

The sun is rising or setting at the given time at the places thus determined, according as t, the hour angle of the sun is between 180° and 360° or 0° and 180°. The eclipse is beginning or ending according as $\cos(\sigma - N)$ is negative or positive.

7. *To find the beginning and the end of the eclipse generally.*

In order to apply the preceding method of determining the rising and setting limits, it is necessary first to find the extreme times between which the time t_0 is to be assumed, or those limits of t_0 between which the solution is possible. The two solutions given by (13) must reduce to a single one when the surface of the cone of shadow has but a single point in common with the earth's surface. Now, the two solutions reduce to one only when $\lambda = 0$, and both values of v become $= M$; but if $\lambda = 0$, then the numerator of the value of $\sin \frac{1}{2}\lambda$ must also be zero; and hence the points of contact are determined by the conditions

$$D + m - \Pi\rho = 0; \qquad D - m + \Pi\rho = 0;$$

or

$$m = \Pi\rho - D; \qquad m = D + \Pi\rho.$$

There may be four cases of contact, two exterior and two interior. The two exterior contacts are the first and last, or the beginning and the end of the eclipse generally. The first interior contact corresponds to the last point on the earth's surface where the eclipse ends at sunrise; the second, to the first point when it begins at sunset. But these interior contacts can occur only when the whole of the shadow on the principal plane falls on the earth.

For the beginning and end generally we have, therefore,

$$(D+\Pi\rho)\,sin\,M=x\,;$$
$$(D+\Pi\rho)\,cos\,M=y.$$

Let T be the time where the conditions are satisfied, and put

$$T=T_0+\tau\,;$$

where T_0 is the epoch of the eclipse tables, for which the values of x and y are x_0 and y_0. Then

$$x=x_0+x'\tau\,; \qquad y=y_0+y\,\tau.$$

Putting

$$\left.\begin{array}{ll} m_0\,sin\,M_0=x_0\,; & n\,sin\,N=x' \\ m_0\,cos\,M_0=y_0\,; & n\,cos\,N=y' \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots(15)$$

the above conditions become

$$(D+\Pi\rho)\,sin\,M=m_0\,sin\,M_0+\tau.\,n.\,sin\,N\,;$$
$$(D+\Pi\rho)\,cos\,M=m_0\,cos\,M_0+\tau.\,n.\,cos\,N\,;$$
$$(D+\Pi\rho)\,sin\,(M-N)=m_0\,sin\,(M_0-N)\,;$$
$$(D+\Pi\rho)\,cos\,(M-N)=m_0\,cos\,(M_0-N)+n\,\tau\,;$$

so that, if we put $M-N=\psi$, we have

$$\left.\begin{array}{l} sin\,\psi=\dfrac{m_0\,sin\,(M_0-N)}{D+\Pi\rho} \\ \tau=\dfrac{D+\Pi\rho}{n}\,cos\,\psi-\dfrac{m_0}{n}\,cos\,(M-N) \\ T=T_0+\tau \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots(16)$$

in which $cos\,\psi$ may be taken with either the negative or the positive sign.

For the two interior contacts we have—

$$\left.\begin{aligned} \sin\psi &= \frac{m_0 \sin(M_0-N)}{\Pi\rho-D} \\ \tau &= \frac{\Pi\rho-D}{n}\cos\psi - \frac{m_0}{n}\cos(M_0-N) \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots(17)$$

For the first approximation we take the mean value of ρ, x', and y', for the assumed time near the conjunction. With the value of τ, thus found, we can repeat the calculation.

8. *Interior contacts.*—When interior contacts exist, the rising and setting limits form two distinct closed curves on the earth's suface. Here, the value of $\sin\psi$ must be real, that is, $\Pi\rho-D$ must be greater than $m_0 \sin(M_0-N)$.

When interior contacts do not exist, the rising and setting limits meet and form a single curve, extending throughout the whole eclipse. The form of this curve may be compared to that of the figure 8 much distorted. Here the value $\sin\psi$ will become impossible, that is $\Pi\rho-D$ is less than $m_0 \sin(M_0-N)$. Hence

when $\Pi\rho-D > m_0 \sin(M_0-N)$, the rising and setting limits form two distinct curves;

when $\Pi\rho-D < m_0 \sin(M_0-N)$, the rising and setting limits form the figure of an 8 much distorted.

9. *To find the curve of maximum obscuration in the horizon.*

The maximum of obscuration depends on the minimum value of the apparent angular distance of the centres of the sun and the moon. Since the measure of this angular distance differs very little from the quantity D, we may consider the maximum of the eclipse as the minimum time of D without sensible error. This condition is

$$\frac{dD}{dT}=0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(18)$$

or putting—

$$\left.\begin{aligned} \sin\sigma\,\frac{dD}{dT}+D\cos\sigma\,\frac{d\sigma}{dT} &= n\sin N-\Pi\rho\,k'\cos\varphi'\cos t \\ &= n'\sin N' \\ \cos\sigma\,\frac{dD}{dT}-D\sin\sigma\,\frac{d\sigma}{dT} &= n\cos N-\Pi\rho\,k'\cos\varphi'\sin\delta'\sin t \\ &= n'\cos N' \end{aligned}\right\}\quad(19)$$

we have from (18)

$$\begin{aligned} \frac{dD}{dT} &= n\cos(\sigma-N') \\ &= n\cos(\sigma-N)-k'\,\Pi\rho\cos\varphi'(\sin\sigma\cos t+\cos\sigma\sin t\sin\delta')=0\,; \end{aligned}$$

or $\qquad \cos(\sigma-N')=0\,;$

that is, $\qquad \sigma-N'=\psi\,(say)=90^\circ$ or 270° .. .. (20)

Substituting this value of σ in the fundamental equations of eclipses, together with the condition that the sun is in the horizon, we get

$$\left.\begin{aligned} D\sin(\pm 90^\circ+N') &= \pm D\cos N'=m\sin M-\Pi\rho\sin v \\ D\cos(\pm 90+N') &= \mp D\sin N'=m\cos M-\Pi\rho\cos v \end{aligned}\right\}\ldots\ldots(21)$$

where

$$\left.\begin{aligned} x &= m\sin M \\ y &= m\cos M \end{aligned}\right\}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(22)$$

whence

$$0=m\cos(M-N')-\Pi\rho\cos(v-N')\,;$$

$$D=m\sin(M-N')-\Pi\rho\sin(v-N')\,;$$

therefore, putting $\qquad \psi=v-N',\quad$ we have

$$\left.\begin{aligned} \cos\psi &= \frac{m}{\Pi\rho}\cos(M-N') \\ D &= m\sin(M-N')-\Pi\rho\sin\psi \end{aligned}\right\}\ldots\ldots\ldots\ldots(23)$$

There will be two values of ψ, since we may take $\sin\psi$ with the

positive or the negative sign, but that value of ψ which would give D greater than $r+r'$ must be excluded.

For the computation, first assume $N'=N$, and with the mean value of ρ calculate v. This value of v will give a more accurate value of N' from

$$\left.\begin{aligned} n' \sin(N'-N) &= +k' \Pi\rho \sin\delta' \cos(v-N) \\ n' \cos(N'-N) &= \quad n-k' \Pi\rho \sin\delta' \sin(v-N) \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots(24)$$

which can easily be derived from (3) and (19)

From N' we can derive v, which will give φ and t.

10. *To find the northern and southern limits of the eclipse.*

This is fully treated in the work of Sawitsch.

11. *To find the extreme times between which the solution is possible.*

It is evident that the first and last points of the curve are those for which $\cos z'=0$. These points are also the first and last points of the curve of maximum obscuration in the horizon, and therefore, the limiting times are here the same as for that curve. If, however, we wish to determine these limiting times independently, the following approximative process will give them, with all the precision necessary.

Since $\cos z'=0$ and $\sigma-N'=\pm 90°$, we get

$$\left.\begin{aligned} \xi &= \Pi\rho \sin v = x \mp D \cos N' \\ \eta &= \Pi\rho \cos v = y \pm D \sin N' \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(25)$$

Let the required time be denoted by $T=T_0+\tau$, T_0 being an assumed time near the middle of the eclipse;

let x_0, y_0 be the values of x and y for the time T_0, respectively,

x', y' ,, ,, mean hourly changes of x and y, respectively,

c', s' ,, ,, ,, ,, ,, ,, $\cos N'$ and $\sin N'$, respectively.

Then $\quad x=x_0+x'\tau\,; \quad \cos N'=\cos N_0+c'\tau\,;$

$\quad y=y_0+y'\tau\,; \quad \sin N'=\sin N_0+s'\tau.$

Substitute these values in (25) and putting

$$\left.\begin{aligned} m \sin M &= \frac{1}{H\rho}(x_0 \mp D \cos N_0) \\ m \cos M &= \frac{1}{H\rho}(y_0 \pm D \sin N_0) \\ l \sin L &= \frac{1}{H\rho}(x' \mp D c') \\ l \cos L &= \frac{1}{H\rho}(y' \pm D s') \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots(26)$$

we get, as usual, solving the equations for τ,

$$\left.\begin{aligned} v - L &= \psi \\ \sin \psi &= m \sin (M - L) \\ \tau &= \frac{\cos \psi}{l} - \frac{m}{l} \cos (M - L) \\ T &= T_0 + \tau \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots(27)$$

in which $\cos \psi$ is to be taken positive or negative for the first or second point, respectively.

To find the latitude and longitude of these extreme points, take $v = L + \psi$ and proceed as before.

12. *To find the curve of central eclipse.*

This curve contains all those points of the surface of the earth through which the axis of the cone of shadow passes. The condition for the central eclipse is

$$D = 0.$$

Then

$$\left.\begin{aligned} x &= \xi = H \cos \varphi_1 \sin t \\ y &= \eta = H\,[(1-c) \sin \varphi_1 \cos \delta' - \cos \varphi_1 \sin \delta' \cos t] \end{aligned}\right\} \quad \ldots\ldots(28)$$

The following formulæ will give the required places—

$$\left.\begin{array}{l}
\left.\begin{array}{l} l\cos\delta_1=(1-c)\cos\delta' \\ l\sin\delta_1=\qquad\sin\delta' \end{array}\right\} \\
\sin B=\dfrac{x}{\Pi};\quad \cos\varphi_1\sin t=\sin B \\
\cos B\sin A=\dfrac{y}{\Pi l};\quad \cos\varphi_1\cos t=\cos B\cos(A+\delta_1) \\
\cos B\cos A=\cos z';\ \sin\varphi_1\qquad=\cos B\sin(A+\delta_1) \\
\tan\varphi=\dfrac{\tan\varphi_1}{1-c}\qquad\qquad L=t-T_0+e
\end{array}\right\}\cdots\cdots\cdots(29)$$

13. *To find the time of the beginning and end of central eclipse upon the earth.*

Here the cone of the umbra touches the earth and the central eclipse is observed at sunrise and sunset, respectively, that is, $\cos z'=0$; or, by (3) and (28),

$$\left.\begin{array}{l} x=\Pi\rho\sin v \\ y=\Pi\rho\cos v \end{array}\right\}\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(30)$$

This is the condition to be satisfied by x and y.

Let T_0 be an arbitrarily assumed epoch;

$T=T_0+\tau$ be the required time of beginning or ending;

x' y' be the mean hourly changes of x and y.

Then,

$$x_0+x'\tau=\Pi\rho\sin v$$

$$y_0+y'\tau=\Pi\rho\cos v$$

Hence, putting

$$\left.\begin{array}{ll} m\sin M=\dfrac{x_0}{\Pi\rho} & n\sin N=\dfrac{x'}{\Pi\rho} \\ m\cos M=\dfrac{y_0}{\Pi\rho} & n\cos N=\dfrac{y'}{\Pi\rho} \end{array}\right\}\cdots\cdots\cdots\cdots\cdots\cdots(31)$$

we get, as usual,

$$\left.\begin{aligned} \psi &= v - N \\ \sin\psi &= m \sin(M-N) \\ \tau &= \frac{1}{n}\cos\psi - \frac{m}{n}\cos(M-N) \\ T &= T_0 + \tau \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots(32)$$

in which $\cos\psi$ is to be taken with the negative sign for the beginning and the positive sign for the end.

The longitude and latitude of these extreme points may be found from (29), by putting $\cos z' = 0$ or $A = 90°$.

14. *To find the duration of total or annular eclipse.*

Let

$T =$ the time of central eclipse

$\tau =$ the duration of total or annular eclipse

then $T' = T \mp \frac{1}{2}\tau$ is the time of beginning or end.

Let x', y', ξ', η' be hourly changes of x, y, ξ, η, respectively.

At the time T', we have by (4)

$$D \sin\sigma = x \mp \frac{1}{2} x'\tau - \left(\xi \mp \frac{1}{2}\xi'\tau\right);$$

$$D \cos\sigma = y \mp \frac{1}{2} y'\tau - \left(\eta \mp \frac{1}{2}\eta'\tau\right).$$

But we have $\quad x = \xi \quad y = \eta\,; \quad$ hence

$$D \sin\sigma = \mp(x' - \xi')\frac{\tau}{2};$$

$$D \cos\sigma = \mp(y' - \eta')\frac{\tau}{2};$$

where
$$\left.\begin{aligned} D &= r - r'(1 - \rho \sin\pi \cos z') && \text{for the total eclipse} \\ D &= r'(1 - \rho \sin\pi \cos z') - r && \text{,, ,, annular ,,} \end{aligned}\right\} \quad \ldots(33)$$

Since
$$x'-\xi'=n' \sin N',$$
$$y'-\eta'=n' \cos N',$$
we have
$$\tau=2\frac{D}{n'} \quad \text{.....(34)}$$

15. *To find the northern and southern limits of total eclipse.*

We may compute this curve by the previous method by simply putting in D the proper value for the total or annular eclipse. But it is more convenient to deduce these points from the previously computed curve of central eclipse. The co-ordinates of the points on the central curve corresponding to the time T being $\xi=x$ $\eta=y$, those for a point on the limiting curve may be denoted by $x+dx$ and $y+dy$, because the two limiting curves of total or annular eclipse lie very near to the central curve. These being substituted for ξ and η in the equations
$$\xi=x\mp D \cos N';$$
$$\eta=y\pm D \sin N';$$
we have
$$\left.\begin{aligned} dx&=\mp D \cos N' \\ dy&=\pm D \sin N' \end{aligned}\right\} \quad \text{.....(35)}$$

Let us now differentiate the following equations
$$\frac{x}{H\rho}=\cos \varphi' \sin t\,; \quad \frac{y}{H\rho}=\sin \varphi' \cos \delta'-\cos \varphi' \sin \delta' \cos t.$$
Then, since we have $\qquad dt=dL,$
$$\frac{dx}{H\rho}=-\sin \varphi' \sin t\, d\varphi'+\cos \varphi' \cos t\, dL\,;$$
$$\frac{dy}{H\rho}=(\cos \varphi' \cos \delta'+\sin \varphi' \sin \delta' \cos t)\, d\varphi'+\cos \varphi' \sin \delta' \sin t\, dL.$$

But by (3)

$$\cos z' = \sin \varphi' \sin \delta' + \cos \varphi' \cos \delta' \cos t\,;$$

hence

$$\Pi\rho \cos z'\, d\varphi' = \cos t\, dy - \sin \delta' \sin t\, dx\,;$$

$$\Pi\rho \cos z'\, dL = \sin t \tan \varphi'\, dy + (\cos \varphi' \cos \delta' + \sin \varphi' \sin \delta' \cos t) \frac{dx}{\cos \varphi'}\,.$$

Substitute the values of dx and dy from (35) in the above expressions, and let h and H be determined by the formulæ

$$\left.\begin{aligned} h \sin H &= \sin N' \\ h \cos H &= \cos N' \sin \delta' \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (36)$$

then, we get, finally,

$$\left.\begin{aligned} \pm \cos z'\, (\rho\, d\varphi') &= + \frac{D}{\Pi} h \sin (H + t) \\ \pm \cos z'\, dL &= - \frac{D}{\Pi\rho} [h \cos (H + t) \tan \varphi' + \cos \delta' \cos N'] \end{aligned}\right\} \quad \ldots\ldots (37)$$

where $d\varphi = \rho(1 + e^2 \cos^2 \varphi) d\varphi'$, neglecting the term of the fourth order in e. log $(1 + e^2 \cos^2 \varphi)$ may be found from the table III as the argument of φ.

This approximate method is not accurate, when $\cos z'$ is very small, that is, near the extreme points of the curve. These extreme points may, however, be determined from formulæ exactly similar to those for penumbra (§10), of course putting in the value of D, proper for the total eclipse.

TABLE I.

φ_1	$\varphi-\varphi_1$	φ_1	φ_1	$\varphi-\varphi_1$	φ_1	φ_1	$\varphi-\varphi_1$	φ_1
0°,0	0′ 0″	90°,0	15°,0	2′ 53″	75°,0	30°,0	4′ 59″	60°,0
0,5	0 6	89,5	15,5	2 58	74,5	30,5	5 2	59,5
1,0	0 12	89,0	16,0	3 3	74,0	31,0	5 5	59,0
1,5	0 18	88,5	16,5	3 8	73,5	31,5	5 8	58,5
2,0	0 24	88,0	17,0	3 13	73,0	32,0	5 10	58,0
2,5	0 30	87,5	17,5	3 18	72,5	32,5	5 13	57,5
3,0	0 36	87,0	18,0	3 23	72,0	33,0	5 16	57,0
3,5	0 42	86,5	18,5	3 28	71,5	33,5	5 18	56,5
4,0	0 48	86,0	19,0	3 33	71,0	34,0	5 20	56,0
4,5	0 54	85,5	19,5	3 38	70,5	34,5	5 22	55,5
5,0	1 0	85,0	20,0	3 42	70,0	35,0	5 25	55,0
5,5	1 6	84,5	20,5	3 47	69,5	35,5	5 27	54,5
6,0	1 12	84,0	21,0	3 51	69,0	36,0	5 29	54,0
6,5	1 18	83,5	21,5	3 56	68,5	36,5	5 30	53,5
7,0	1 24	83,0	22,0	4 0	68,0	37,0	5 32	53,0
7,5	1 30	82,5	22,5	4 4	67,5	37,5	5 33	52,5
8,0	1 35	82,0	23,0	4 9	67,0	38,0	5 35	52,0
8,5	1 41	81,5	23,5	4 13	66,5	38,5	5 37	51,5
9,0	1 47	81,0	24,0	4 17	66,0	39,0	5 38	51,0
9,5	1 53	80,5	24,5	4 21	65,5	39,5	5 39	50,5
10,0	1 58	80,0	25,0	4 25	65,0	40,0	5 40	50,0
10,5	2 4	79,5	25,5	4 29	64,5	41,0	5 42	49,0
11,0	2 10	79,0	26,0	4 32	64,0	42,0	5 43	48,0
11,5	2 15	78,5	26,5	4 36	63,5	43,0	5 45	47,0
12,0	2 21	78,0	27,0	4 40	63,0	44,0	5 45	46,0
12,5	2 26	77,5	27,5	4 43	62,5	45,0	5 45	45,0
13,0	2 32	77,0	28,0	4 46	62,0			
13,5	2 37	76,5	28,5	4 50	61,5			
14,0	2 42	76,0	29,0	4 53	61,0			
14,5	2 48	75,5	29,5	4 56	60,5			
15,0	2 53	75,0	30,0	4 59	60,0			

TABLE II.

δ'	$log\ l$	$\delta_1-\delta'$	δ'	$log\ l$	$\delta_1-\delta'$	δ'	$log\ l$	$\delta_1-\delta'$
0°	9,998 55	0′ 0″	8°	9,998 57	1′ 35″	16°	9,998 66	3′ 03″
1	55	0 12	9	58	1 47	17	67	3 13
2	55	0 24	10	59	1 58	18	69	3 23
3	55	0 36	11	60	2 10	19	70	3 33
4	55	0 48	12	61	2 21	20	72	3 42
5	56	1 0	13	62	2 32	21	73	3 51
6	56	1 12	14	63	2 42	22	75	4 00
7	57	1 24	15	64	2 53	23	77	4 09
8	9,998 57	1 35	16	9,998 66	3 03	24	9,998 79	4 17

TABLE III.

φ	$log(1+e^2cos^2\varphi)$	φ	$log(1+e^2cos^2\varphi)$	φ	$log(1+e^2cos^2\varphi)$	φ	$log(1+e^2cos^2\varphi)$
0°	0,00 289	24°	0,00 241	48°	0,00 130	72°	0,000 28
2	289	26	233	50	120	74	22
4	287	28	225	52	110	76	17
6	286	30	217	54	100	78	13
8	284	32	208	56	090	80	09
10	280	34	199	58	080	82	06
12	277	36	189	60	072	84	03
14	272	38	179	62	064	86	01
16	267	40	170	64	056	88	00
18	262	42	160	66	048	90	0,000 00
20	255	44	150	68	041		
22	249	46	140	70	034		
24	0,00 241	48	0,00 130	72	0,00 028		

How Mercurous and Mercuric Salts change into each other.

By

Seihachi Hada, *Rigakushi.*

College of Science, Imperial University.

Notwithstanding all that has been done and observed about the passage of mercurous salts into mercuric, and, conversely, of these into mercurous salts, in the absence of specific oxidising and reducing agents, or, as we are apt to say, 'spontaneously,' the subject seemed to call for a comprehensive investigation, which should serve to establish the way or ways in which these changes come about.

It is rare to meet with a definite general statement on the subject. Mendeléeff's *Principles of Chemistry* contains one which runs as follows: "The mercurous compounds under the action of oxidising "agents, even air, pass into mercuric compounds, especially in the "presence of acids, but the mercuric compounds when in contact with "mercury, change more or less readily, and turn into mercurous "compounds" (vol. ii, p. 50). Another occurs in Gmelin-Kraut-Jörgensen's *Handbuch* (not Gmelin-Watts'), which is to the effect that water "decomposes mercurous salts in the heat into metal and mercuric salts," and one similar is to be found in Menschutkin's *Analytical Chemistry.* These sentences express probably the current belief of chemists; to what extent they are sufficient and accurate will appear in this communication, except as to the effect of oxidising agents other than air, upon which I have nothing to say.

The work now to be recorded proves the truth of two propositions as to the nature of the changes of mercurous and mercuric salts into

each other ; one, first in interest and importance, is that all mercurous salts dissociate, in the strict sense of this term, into mercury and mercuric salts, in presence of water ; and, reciprocally, that all mercuric salts combine with mercury, in presence of water, to form mercurous salts, when these have any existence. Although not generally known, and without having led to the full recognition of that proposition, many observations have already been made by chemists and pharmacologists working upon the salts of mercury, which lend every support to it. Reference to these observations will be made where they become applicable ; here, it is only necessary to state that Rose held so strongly that mercurous salts in solution readily decompose into mercuric salts and mercury, as to deny existence to any precipitated basic mercurous salts, treating the basic part of the precipitates as a mixture of mercuric basic salt and mercury, the other part being sparingly soluble normal mercurous salt. His right view of the case was thus based on a wrong apprehension of some of the facts. It seems proper for me to mention that only after I had discovered for myself the facts described in this paper was I able to make anything of the confused records of them to be found in chemical literature.

In accordance with the laws of dissociation, decomposition of mercurous salts into mercury and mercuric salts increases with rise of temperature and only progresses freely so long as the mercury set free is continuously removed from the field ; and, conversely, combination of mercuric salts with mercury only becomes complete in presence of excess of the metal and at lower temperatures,unless the mercurous salt produced is insoluble and thus goes out of the field, as in the case of the chloride. Combination with mercury does not occur at all when the mercurous salt is incapable of existing, as is the case with the cyanide, with the sulphide, with double sulphites, thio-

sulphates, thiocyanates, oxalates, and iodides, and with all ammoniated salts, or, again, when the mercurous compound is one which freely changes, such as the oxide and the carbonate.

Dissociation of mercurous salts into mercury and mercuric salts in the presence of water is caused not only by an elevated temperature, but by light also, even at the common temperature, and apparently in all salts.

The other proposition established in this paper is that some, anp probably all, mercurous salts are oxidisable by air, in presence of water, when the temperature is much above 100° ; and that at and below that temperature mercurous salts are not oxidisable in the air, or, if they are, then so slowly that any effect of their oxidation is not recognisable through being lost, by its smallness, in the effects of dissociation. Mercurous oxide alone oxidises at the common temperature ; this fact and that mercury itself does not, were established by Barfoed in 1883, Berthelot's assumption that mercury is slightly oxidisable being, as Barfoed shows, based on wrong apprehension of facts observed by him.

Besides the two propositions substantiated by the present work upon the interconvertibility of the two series of mercury salts, the fact has been ascertained of there being another way in which mercurous nitrate becomes a mercuric salt spontaneously, in presence of water, which is that it is converted into mercuric nitrite and nitrate, both by heat and by light. In so far as this is a case of the oxidising action of nitric acid (namely, of that produced by the action of water on the salt or else that added to prevent the formation of basic salts), its occurrence is nothing new. But, under the circumstances, it is remarkable and calls for consideration. One per cent. of nitric acid in a ten per cent. solution of mercurous nitrate is amply sufficient to keep away basic salts, even after much mercuric salt has been produced, and a much stronger solution of the acid has no action upon mercurous

nitrate in the dark, even at 100°. But either at 150°, and then in a few hours ; or, at the common temperature in strong daylight, slowly in the course of days, though at a rate growing with the duration of the experiment, a large fraction of the mercurous salt can become mercuric, without separation of mercury.

In analysing this change, it seems right to admit that nitrous acid is essential to start the action, that traces of this acid are generated by the heat or light, even in such weak nitric acid, and also that the dissociation of the mercurous nitrate is caused by the same agency. The ultimate change is represented by—

$$(HgNO_3)_2 + 3HNO_3 = 2Hg(NO_3)_2 + HNO_2 + H_2O\ ;$$

but this includes those of

$$(HgNO_3)_2 = Hg + Hg(NO_3)_2\ ;$$

$$Hg + HNO_3 + HNO_2 = Hg(NO_2)_2 + H_2O\ ;$$

$$Hg(NO_2)_2 + 2HNO_3 = Hg(NO_3)_2 + 2HNO_2\ ;$$

the increase in nitrous acid being the cause of acceleration of rate of change.

Mercury nitrates.

Conversion of mercuric nitrate to mercurous nitrate.—A solution of mercuric nitrate shaken violently for a very short time with large excess of mercury is fully converted into one of mercurous nitrate. This simple and perfect method of making a solution of mercurous nitrate, free from nitrous acid, has been in use in this laboratory for years. The solution of mercuric nitrate may be as weak as may be desired, but it should not contain much more than 10 per cent. of metal, for this becomes doubled in the process. The violent shaking is conveniently carried out in a stoppered bottle.

(*Literature*).—What has long been known and recorded of the possibility of combining mercuric nitrate with mercury is this. Bucholz (1810), for the preparation of mercurous nitrate, directs (according to Gmelin's *Handbook*) that the mixture of basic mercurous and mercuric nitrates, obtained by dissolving mercury in strong nitric acid and evaporating to dryness, shall be triturated with mercury and a little water, and the product be dissolved in hot water and a little nitric acid. Lefort (1845 ; *Annalen*, **56**) says that it is true that mercuric nitrate, occurring along with mercurous nitrate, may be converted into mercurous salt by boiling the dilute solution with mercury, but that the boiling must be long continued. In a paper on mercurous oxide ('The behaviour of mercurous salts with soda' ; in Danish, 1883 ; *J. pkt. Ch.* 1888) Barfoed mentioned the fact that mercuric nitrate solution dissolves finely divided mercury. But so little has this fact been generally known that, for instance, Bruns and von der Pfordten in 1888 (*Berichte*) showed themselves to be unaware of it. Nowhere does it appear to be known that, in a few minutes, mercuric nitrate can be fully converted into mercurous nitrate by violently shaking its cold solution with excess of liquid mercury.

The stability of mercurous nitrate.—Before treating of the ways in which mercurous nitrate passes into mercuric nitrate, something has to be said as to its stability. It must be a matter of common observation that, as Gmelin-Kraut-Jörgensen's *Handbuch* states, mercurous nitrate kept for some time becomes yellow through partial oxidation. But this, I have found, is not true of the carefully prepared salt. As Marignac pointed out (1849), its crystals usually enclose mother-liquor, and this is strongly acid. By selecting small clear crystals, or crushing large ones, and thoroughly pressing in filter paper, the salt is obtained in a stable condition. If it is to be kept, as usual, in a bottle,

it had better be exposed for a time in a desiccator before storing it. It has been found to keep quite unchanged, or, when a little effloresced and faintly yellowish, to be still free from mercuric salt. Crystals, after pressing in paper, have been left in a basin exposed to the air, but covered from the entrance of dust, and after the lapse of a full year and through wide ranges of temperature and moisture, have remained almost unchanged ; some of the crystals had remained clear, some had become opaque, while all had become very slightly brown owing probably only to hydrogen sulphide, while even the opaque crystals hardly showed the presence of any mercuric salt. Well cleansed and effloresced mercurous nitrate kept in a bottle has always a peculiar ozone-like odour, according to my experience.

A solution of mercurous nitrate, free from nitrous acid and in a closed vessel, appears to be quite stable while kept in the dark.

Decomposition of mercurous nitrate by water.—When normal mercurous nitrate has been freed with care from its acid mother-liquor, it is always decomposed by water and in such a way as to give an acid solution and a precipitate of basic mercurous nitrate. I have been unable to get the salt to dissolve completely in a little warm water, as it is stated to do in Gmelin's *Handbook* and some later works, except where the crystals had been little more than drained from their mother-liquor. Even after the acid solution and the basic salt have been kept for some hours in an open vessel at or about 100°, but not in a strong light, the basic salt (of a dull yellow colour) still remains essentially free from mercuric salt, although the solution now contains it in consequence of dissociation, as will be presently described. Rose in 1841 (*Annalen* **39**, 106) described such a basic precipitate as a mixture of basic mercuric salt, mercury, and unchanged normal mercurous nitrate, combatting the notion that any insoluble basic mercurous salts exist. It would be difficult to prove the precipitate to be altogether

free from mercuric salt, because it cannot be asserted that a very little, if present, would not have become again mercurous in contact with mercury in the act of dissolving in dilute nitric acid. But it is certainly a mistake to hold, with him, that mercuric oxide, as the weaker base, is to be found in the precipitate and not in the mother-liquor. The precipitate can, indeed, be easily rendered mercuric by pouring off its mother-liquor and heating it several times with fresh water, a fact pointed out by Kane (1838). It then becomes more and more basic by loss of acid and highly mercuric, no doubt, now by dissociation.

Dissociation of mercurous nitrate by heat.—I do not wish to affirm that the dissociation of mercurous nitrate does not go on slowly at the common temperature in the absence of light ; it may do so, but so slightly as to escape detection. It does not follow that it does do so, because of its dissociation at temperatures not much above the common, for, while hot mercury oxidises, there is conclusive evidence that cold mercury does not (Barfoed). The experiments now to be described exhibit dissociation occurring at slightly elevated temperatures in the dark.

About one gram of normal hydrated mercurous nitrate, free both from metallic mercury and from mercuric nitrate, was put with 10 cc. of water in an Erlenmeyer flask, in order that its solution might present a relatively large surface for evaporation. A reflux condenser was connected with the flask to prevent loss by this evaporation and a gentle current of carbon dioxide was maintained during the heating of the flask, in order to keep air out. The flask was kept immersed in boiling water and before very long a lustrous very thin film of mercury could be seen in the lower part of the condenser-tube, which had become a coating of globules in two hours, when the heating was stopped. The metallic mercury was brushed out of the tube into a capsule and most of the solution in the flask decanted from the

precipitated basic salts, which were visibly mixed with a few minute globules of metal, evidently fallen down from the condenser tube. The basic salts were dissolved in a little very dilute nitric acid, their solution was quickly poured off from the mercury and added to the main quantity of solution, and the mercury was weighed with that removed from the condenser. Mercurous chloride was precipitated from the cold solution by sodium chloride and removed, and then mercuric sulphide was precipitated from the filtrate and weighed. It was equal to 0.0378 gram of mercury, while that obtained as metal weighed 0.0392 gram, and therefore the same within limits of experimental error.

The last experiment was repeated but with two modifications. The solution was kept in gentle ebullition by a small gas-flame, and no carbon dioxide was passed through the flask, the steam of the boiling solution being relied upon to keep out air. The mercury found as mercuric salt weighed, this time, 0.0913 gram and that as metal 0.0946 gram.

A third experiment was made, like the last, but with the modification of adding at the beginning just enough nitric acid, (included in the 10 cc.) to keep all the mercurous salt in solution. Everything but precipitation of basic salts went on as before, the mercury volatilised was 0.0345 gram, and that of the mercuric nitrate 0.0415, the latter being probably not more than equivalent to the metallic mercury, if all had been collected, only 7 mgm. being wanted.

Three parallel experiments were then made, the duration of heating being eight hours, and boiling water the source of heat. Through the first flask a gentle flow of carbon dioxide was kept up, and through the other two a gentle flow of air. Just enough nitric acid to prevent basic salt precipitating was added to the contents of the third flask, in place of part of the 10cc. of water alone used in the first and second

flasks. The products were :—where carbon dioxide was used, metallic mercury, 0.1191 gram, mercuric radical, 0.1213 gram ; where air was passed and no nitric acid added, metallic mercury, 0.1195 gram, mercuric radical, 0.1202 gram ; where air was passed and nitric acid added, metallic mercury, 0.1104 gram, mercuric radical, 0.1066 gram. That in the last case the very little nitric acid added played no part as an oxidising agent was further shown by titrating for free acid after the sodium chloride had been added, and finding the acidity closely equivalent to that of the nitric acid which had been added.

Thus, in eight hours at or near 100°, one third of the mercurous nitrate had decomposed into mercuric nitrate and metal in the two experiments made without addition of nitric acid, and not much less in the third experiment where this acid was present. Further, in eight hours at 100° in a current of air no sensible oxidation of mercurous nitrate by air or nitric acid had taken place.

Literature and criticism.—Gmelin tells us that "The solution of this salt [mercurous nitrate in presence of a little nitric acid], when exposed to the air takes up oxygen and is converted into mercuric nitrate ; the same change is produced by continued boiling, mercury being then given off together with the water (Proust). This is very confusing. From it, however, may be seen that Proust (1816) knew that mercurous nitrate exposed to the air in solution was partly converted to mercuric nitrate, and that on boiling its solution mercury itself volatilised with the steam. But, as is shown in this paper, the mercuric nitrate is not produced by oxidation, at least, not to any sensible extent. Proust seems, further, not to have put the natural interpretation upon the facts which he had observed, namely, that mercurous nitrate decomposes (dissociates) into mercuric nitrate and mercury, and, after having been once recorded in Gmelin's *Handbook*, the facts pointing to this decomposition ceased to be mentioned or re-

cognised. Thus, in the *Kraut-Jörgensen* edition (1875), we are only told, with Proust as authority, that the solution of mercurous nitrate oxidises in the air, the record of the volatilisation of mercury being suppressed, while the error as to oxidation is retained. The fact of the volatilisation of mercury appears in none of the modern dictionaries or handbooks. It is probably on the authority of Proust that Mendeléeff has stated, in the passage already quoted, that mercurous salts, particularly in acid solutions, are oxidisable by the air. Kane (1838; *Annalen*, **26**; *Ann. Chim. Phys.* [2], **72**, 215) observed that half basic mercurous nitrate is partly converted by long boiling with fresh quantities of water into mercury and mercuric salt, the volatilisation of the mercury not being noticed by him. Rose's views (1841; *Annalen*, **39**, 106) have already being referred to. He is clear on the point that mercurous nitrate, continuously boiled with water, becomes mercuric nitrate and mercury, but his purely theoretical paper contains other statements which cannot be accepted. According to him, both the mercury and the mercuric nitrate occur in the precipitate which water forms from mercurous nitrate, but that is clearly not the case. Gmelin on his own authority (*Handbook*) makes a statement which, for the unfortunate reader, serves fully to efface any impression caused by Kane's statement given above, for he tells us, "On boiling the monobasic [normal] salt with water till the residue turns grey, the filtrate contains but a mere trace of mercuric salt." This is no misprint; it is repeated in *Gmelin-Kraut*. I had better, therefore, at the cost of repetition, state here that in an open vessel of good modern glass or porcelain, mercurous nitrate boiled with water for hours produces mercuric nitrate in solution, mercury vapour, usually no globules under the solution, and a basic mercurous precipitate which does not become grey when strong day-light is excluded, but remains dull yellow with perhaps a tinge of green; as before stated, the

solution must not be poured off and replaced by water, but the loss of water by evaporation be made good from time to time.

Another instance of ill-defined and, therefore, unavailable information concerning the behaviour of mercury nitrates on boiling them in water is to be found in *Pogg. Ann.*, 66, where Brooks, who prepared a mercurous-mercuric nitrate, is made to say that in the air mercurosic nitrate boiled with water becomes mercurous nitrate in solution, and mercuric oxide and mercury metal separated; while with exclusion of air mercuric nitrate goes into solution, along with traces of mercurous nitrate, leaving a residue of both oxides.

Dissociation of mercurous nitrate by light.—Although dissociation of mercurous nitrate in cold solution may be assumed to be caused by the action of light, its occurrence has not been experimentally established, because of the interference of the effects of light upon the nitric acid. It may, however, be mentioned that strong daylight soon darkens basic mercurous nitrate as it lies under its mother-liquor, and such an effect in the case of some mercurous salts is certainly one of dissociation.

Oxidation of mercurous nitrate by oxygen at 150°.—A gram of mercurous nitrate was heated at 150° for six hours with water 10cc., in a sealed tube, the air in which had been displaced by oxygen, to represent condensed air in the small space available. Much of the oxygen was absorbed and 6.5 per cent. of the mercurous nitrate converted to mercuric salt, partly in solution, partly in form of brilliant yellow crystals of basic salt (both mercurous and mercuric).

Another gram was heated in oxygen for five hours, but this time all in solution in 10cc. of one per cent. nitric acid. In this experiment more than 28 per cent. of the mercurous salt became mercuric nitrate. Much oxygen had been absorbed and no nitric acid had been reduced.

In a third experiment the mercurous nitrate was heated to 150° with water only, for five hours, in an atmosphere of carbon dioxide. It underwent no change beyond slight dissociation. Dissociation in a sealed tube is impeded by the retention of the mercury vapour. Very different was the result in an atmosphere of carbon dioxide when a little nitric acid had been added, as will presently be described. In the above cases, the nitric acid may have assisted as a carrier of the gaseous oxygen, but as other mercurous salts are also oxidisable at 150°, this possible assistance may be left out of consideration.

Mercurous nitrate not sensibly oxidised by air at lower temperatures.—In the experiments exhibiting the dissociation of mercurous nitrate at 100° and even a little higher, any oxidation by the passing current of air did not betray itself; for as much mercuric nitrate was produced in a current of carbon dioxide or an atmosphere of steam. Also, at the common temperature, in the dark, a solution of mercurous nitrate remains unchanged even in an atmosphere of oxygen. But, since experiments made long ago by Mialhé have been accepted as establishing the oxidisability of wet mercurous chloride by air at only a slight elevation of temperature, it will be well to give the result of a modification of his experiment, applied in such a way as to test the point in the case of mercurous nitrate. His method consisted in comparing the changes that went on in a closed vessel with those in an open vessel in a current of air, while his results were the production of much more mercuric salt in the latter case. The experiments now to follow were hardly necessary, because Mialhé's results are only in accordance with the occurrence of dissociation, but it seemed well to make them.

Two small flasks were provided and into each were put 1.5 grams mercurous nitrate and 15cc. water. One flask was closed by

a cork, while the other was provided with a reflux condenser and a tube to lead carbon dioxide through the solution. The flasks were placed side by side in an oven and were kept there for about 45 hours at a temperature of 45-47°, while carbon dioxide was continuously bubbled through the solution and precipitate in one of the flasks. On examination, the contents of the flask containing air enclosed gave 0.0040 gram mercuric sulphide and those of the flask kept all the time in a continually renewed atmosphere devoid of oxygen gave 0.0107 gram mercuric sulphide or 2½ times more than the other. Had the current of gas been one of air it might have been supposed to have caused oxidation, but, as the experiment was conducted, the effect could only be due to the carrying off of mercury vapour by the current of chemically inactive gas.

The experiment was repeated, using in each flask 2 grams mercurous nitrate, 20cc. water, and a little dilute nitric acid. The temperature was 45-50° and the time was extended to 75 hours. The result was: mercuric sulphide obtained from the closed flask 0.0082 gram; from the flask through which carbon dioxide had streamed, 0.028 gram, or nearly 3½ times as much.

A similar experiment performed at a little lower temperature, 20-30° and lasting 50 hours gave quantities of mercuric sulphide too small to weigh, but the blackening by hydrogen sulphide of the mother-liquor of the precipitate caused by sodium chloride was far stronger where carbon dioxide had been passed all the time than where the solution had been corked up with the air in the flask.

Mercurous nitrate changed by heat to mercuric salt by reduction of nitric acid.—In a sealed tube and in an atmosphere of carbon dioxide, mercurous nitrate dissolved in one per cent. nitric acid, one gram in 10cc., kept at 150° for five hours, is largely converted into mercuric salt by some of the nitric acid being reduced to nitrous acid. The

atmosphere of the tube liberates iodine from potassium iodide, and the solution precipitated first by sodium chloride, and then by hydrogen sulphide, is milky from sulphur.

Mercurous nitrate changed by light to mercuric salt by reduction of nitric acid.—In a number of small Erlenmeyer flasks a freshly prepared solution of mercurous nitrate dissolved in one per cent. nitric acid was equally distributed, each flask receiving 10cc. solution containing one gram of mercurous nitrate. Most of the flasks were exposed together to strong day-light, the rest were kept in the dark ; other conditions of the flasks varied, as will be described. Along with those exposed to the light were others having the mercurous nitrate with water and no nitric acid added. Some of the flasks had their contents examined at the end of 19 days exposure ; the others at the end of 33 days. The examination consisted in testing for nitrous acid in one tenth of the solution by potassium iodide and starch, and for the quantity of mercuric radical in the other nine-tenths, the mercuric sulphide being washed successively with water, alcohol, and carbon bisulphide. The air or other gas which the flask had been filled with at first, was found apparently unchanged at the end.

Under whatever other condition it had been, the mercurous nitrate which had been exposed to light had in every case generated much nitrous acid, and mercuric salt, while that which had been in the dark showed the presence of neither product in 19 days and only insignificant amounts in 33 days. I believe none is produced ; for, I regret to have to admit, the darkness in which the flasks had been preserved was far from being total.

The difference between closed and open flasks was marked ; the closed flask being closely sealed, the open one with its month under only a cap of filter paper. In the closed flask the mercuric radical was found to be half as great again in 33 days as in the open one.

Evidently, therefore, aerial oxidation plays no sensible part in the conversion of mercurous nitrate to mercuric nitrate.

Oxygen would seem, indeed, to impede the conversion in the absence of basic salt, but not in its presence. For, at the end of 19 days, the conversion to mercuric salt was half as great again in a closed flask in which the air had been replaced by carbon dioxide as it was in a closed flask containing air.

On the other hand, in a flask at the end of 19 days, in which 2 grams mercurous nitrate had been put with 10cc. water in an atmosphere of oxygen itself, there was found just the same quantity of mercuric radical as in the flask holding carbon dioxide. Also in 33 days two flasks, one of which had enclosed carbon dioxide, and the other air, showed the same contents of mercuric radical, a result, which, I consider, is brought into conformity with that obtained in a similar pair of flasks opened in 19 days, by allowing for the consumption of nitric acid, which had taken place, counteracting the impeding action of the oxygen. For, the conversion by light being one in which nitrous acid is formed from the nitric acid, oxygen will oxidise this to nitric acid in acid solution, while it will not oxidise the mercurous nitrite existing as such in the comparative absence of nitric acid.

In these experiments, comparison was also made as to the influence of mercury vapour, which Barfoed has shown to be such a material presence in any atmosphere in contact with mercury. Some of the flasks employed had each a bent tube of good diameter passing through the cork and at its outer end dipping in a vessel of mercury throughout the experiment. The effect was striking where the experiment lasted for 33 days. Whether the atmosphere was air or carbon dioxide, the production of mercuric radical was only two-thirds in a mercurial atmosphere of what it was in a non-mercurial atmo-

sphere. Where the exposure lasted only 19 days, the mercuric radical formed was only five-sixths in the mercurial atmosphere of what it was in the non-mercurial, in those cases where carbon dioxde was used; where air was used, the mercuric radical was only less by a tenth in the mercurial atmosphere than what it was in the absence of mercury. There can hardly be a second opinion as to the manner in which the mercury exercises its inhibitory effect; that this effect should become so manifest is very remarkable. As pointed out in the ntroductory section of this paper, the nitrous acid produced by the light multiplies itself in making mercurous nitrate into mercuric salt. Mercury vapour in the atmosphere over the solution, minute as it is in quantity, is yet large enough, no doubt, to combine with an appreciable fraction of the minute quantities of the nitrite-ion generated by light, and thus reduces the rate of its accumulation. Whether it unites with it to produce mercurous or mercuric nitrite will not be ascertainable, the quantity of salt produced being probably inappreciable. Were it not for the nitrous acid doubling itself in action,—

$$(HgNO_3)_2+HNO_3+HNO_2=Hg(NO_3)_2+Hg(NO_2)_2+OH_2;$$
$$Hg(NO_2)_2+2HNO_3=Hg(NO_3)_2+2HNO_2,$$

its consumption by mercury would be too insignificant to have noticeable effect.

The inhibitory effect of mercury vapour is the same as that of exposure to the open air, the reason being that the nitrous acid, produced by lignt so slowly as it is, gets diffused away in the air and its accumulation impeded. It must be remembered that, in such solutions as those worked upon in these experiments, the amount of free nitrous acid present must always be minute, much the greater part of it being in the form of mercury nitrites, a consideration which will explain the nearness, in amount of effect, of the action of mercury vapour to that of the open air.

Experiments of the present kind must all be made together ; differences in temperature and above all in the intensity of the daylight having great effect. I append my results in a table. I hope to supplement them by further observations in the next winter session. The numbers in the table are the quantities of mercury found as mercuric salt, 0.7143 gram being the total mercury present in each flask, or double that in the case where 2 grams of mercurous nitrate were taken.

With nitric acid.	May 21st. June 23rd.	May 21st. June 9th.	July 3rd. July 23rd.
Open,	.0377	—	—
Closed, air,	.0543	.0145	.0368
Closed, air, mercury,	.0363	.0158	—
Carbon dioxide,	.0542	.0240	—
Carb. diox., mercury,	.0383	.0201	—
Oxygen,*	.0247	.0285	.0324
Oxygen, mercury,*	.0042	.0000	—
Oxygen, in darkness,	.0181	lost	—
Without nitric acid.			
Oxygen (2 gr. salt to 10cc.),	.0690	.0222	—

Mercury sulphates.

Conversion of mercuric to mercurous sulphate.—Although the fact receives little or no attention in text books, it is too well known to

* The results obtained in oxygen are too marked to be relied on, and need confirmation ; one analysis was spoiled New experiments because of their length, are for the present not possible. I hope to make them next session. But it will be observed that the results of the oxygen experiments accord with the inferences I have made, and are only remarkable for their extreme character.

need confirmation that mercuric sulphate and mercury, rubbed together and moistened with water or alcohol and a little sulphuric acid, combine readily, with the evolution of heat. The process is not a convenient one for the preparation of pure mercurous sulphate, though serviceable in the manufacture of calomel and in constructing the Latimer-Clark galvanic cell. It is of great theoretical importance.

Decomposition of mercurous sulphate by water.—It is familiar to every chemist that, whereas mercuric sulphate turns bright yellow on contact with water, mercurous sulphate remains white, even when washed. But it seems to be unknown that there is a limit to this stability quite easy to reach. Apparently, earlier observations of the fact have been set aside as dependent upon the presence of mercuric sulphate in the sulphate worked upon.

Mercurous sulphate was precipitated from a solution of crystals of mercurous nitrate, free from mercuric salt and nitrite, by adding dilute sulphuric acid. It was well washed with water and remained white. Of this moist salt about one gram was strongly shaken with a liter of distilled water. This treatment rendered it distinctly yellow, and repetition of the shaking with a fresh liter of water deepened the colour to a clear though light yellow.

Decomposition of mercurous sulphate by light.—In experimenting with mercurous sulphate and water, as in the above case, light must be avoided. It is known, I believe, that light acts upon mercurous sulphate as it does upon the chloride. Mercurous sulphate when moist becomes dark brown in a strong light. That which has been made yellow by treatment with much water becomes first greenish under the action of daylight and then dark brown. It seems safe to assume that these colour changes are due to dissociation of the mercurous salt into mercuric salt, and mercury or hypomercurous salt. The effect is only superficial and too slight to admit of its nature being tested, besides

that contact with acids must largely if not wholly reverse it.

Dissociation of mercurous sulphate by heat.—Boiled for some hours with water, in the same way as mercurous nitrate, mercurous sulphate was found to be converted, to a small extent, into basic mercuric sulphate, mercury, and sulphuric acid. The mercury was got as a sublimate, the water became acid, and the undissolved sulphate yielded some mercuric chloride when treated with hydrochloric acid.

Oxidation of mercurous sulphate at 150°.—Heated for six hours in oxygen, with water and a little sulphuric acid, in a sealed tube at 150°, one gram of mercurous sulphate gave no mercury, but .0121 gram mercuric radical, indicating the oxidation of 1.5 per cent. of the mercurous sulphate. It should, I think, be taken into account that through insolubility much of the sulphate is kept out of contact with the oxygen, and unacted upon, during the heating in the tube, and the same is true of the phosphate and chloride.

(*Literature*).—Planche's very old process of making calomel has illustrated, for a long time, the union of mercury with mercuric sulphate even before heat is applied. According to Kane, mercurous sulphate is not convertible into basic salt by water. Rose observed the dissociation of mercurous sulphate by boiling it, for a long time, with much water, but he did not get the mercury as a sublimate, as I have done, but along with the basic mercuric sulphate and the unchanged mercurous sulphate. The mercury must have condensed in the upper part of the vessel he used, and then rolled down. Proust and also Donovan are said to have got a yellow residue by boiling mercurous sulphate with water, no mercury being mentioned.

Mercury phosphates.

Conversion of mercuric to mercurous phosphate.—Moist mercuric phosphate triturated with its equivalent of mercury unites with it, growing

warm, and becomes, for the most part, at least, mercurous phosphate.

Moist mercurous phosphate is darkened by light. No attempt was made to decompose it by cold water.

Dissociation of mercurous phosphate by heat.—To obtain a mercurous phosphate free from the nitrate, it was precipitated by adding a solution of mercurous nitrate to a good excess of sodium phosphate in solution acidified with nitric acid, then washed, and dried on a tile. This salt is difficult to decompose into mercury and mercuric phosphate. However, it does dissociate like other mercurous salts. By boiling it for six hours a small sublimate of mercury was obtained and the mercurous phosphate became pale yellow from the presence of basic mercurous phosphate. The water over it had become quite acid, and contained both mercuric and mercurous phosphates dissolved in phosphoric acid, or as acid phosphates. Rose got similar results, except that the mercury was mixed up with the phosphates, but not as a sublimate, which does not accord with my experience. Gerhardt observed that mercurous phosphate heated dry becomes mercuric phosphate and mercury, a fact closely related to my subject, though not actually belonging to it.

Oxidation of mercurous phosphate.—Heated at 150° in oxygen, mercurous phosphate was oxidised much to the same extent as the sulphate.

Mercury acetates.

Conversion of mercuric to mercurous acetate.—A cold dilute solution of mercuric acetate shaken violently with much mercury is readily and at once converted all into mercurous acetate. According to Lefort (1845 ; *Annalen*, 56), this conversion needs long boiling ! I do not hesitate to say that long boiling would never complete it, so easily does mercurous acetate dissociate. The fact that mercuric acetate can be

converted into mercurous acetate is not mentioned in systematic works, so far as I can find.

Dissociation of mercurous acetate by heat.—Mercurous acetate so freely dissociates when boiled with water that the mercury not only volatilises with the steam, but collects in globules under the solution. The undissolved part of the salt and that crystallising out on cooling are a mixture of normal and basic mercurous acetates, while the mother-liquor contains much mercuric acetate. Addition of acetic acid at starting does not sensibly affect the dissociation, though it prevents formation of basic salt.

(*Literature and criticism*).—It has long been widely known, that mercurous acetate yields a little mercury when its solution is boiled. The first definite reference to this fact seems to be that by Berthemot (1848), given in Gmelin's *Handbook*, in connection with the preparation of mercurous iodide. No mention of it is made in the *Organic Part* of the work under mercury acetates, or in Watts's *Dictionary*, or Morley and Muir's *Dictionary*, or Beilstein's *Organic Chemistry*. Berthemot quite definitely states that mercurous acetate is partly decomposed by boiling water into mercury which separates and mercuric acetate which dissolves. Allen Miller, in his *Elements of Organic Chemistry*, (1869), stated that it decomposes into mercury and a sparingly soluble basic acetate, which is unintelligible unless we know that mercuric acetate is also produced. Fresenius in his *Quantitative Analysis*, mentions that mercurous acetate yields a very little mercury when boiled, but fails to add that it does so in a way quite different from that in which mercurous formate yields mercury,—does not mention, in fact, that mercuric salt is formed in the one case and not in the other. Gmelin, who, as just now said, is silent on the subject in his *Organic Chemistry*, and correctly states the facts when describing the preparation of mercurous iodide, records in his description of the

properties of mercurous salts in general, on the authority of Vogel, that sugar boiled with mercurous acetate yields mercury, without mentioning that mercury also precipitates in the absence of sugar or a substitute for it. The fact is that pure cane sugar has no effect. One gram of mercurous acetate was put into 10cc. of water, and one gram of it into 10cc. of a strong solution of sugar ; then both solutions were raised to the boiling point and cooled. Where sugar was absent, .0627 gram mercuric sulphide was precipitated after removal of mercurous salt ; where sugar was present, .0612 gram ; in both cases metallic mercury was liberated apparently to the same extent ; the sugar, therefore, had exerted no influence.

Dissociation of mercurous acetate by light.—It is already known that the acetate among mercurous salts is especially sensitive to light. Some of it was exposed under water in a flask to the sunlight of four days. It was thus strongly blackened, while the solution contained a very evident quantity of mercuric acetate. Another portion kept under water four days in the dark, was scarcely changed in colour.

Oxidation of mercurous acetate.—Mercurous acetate heated to 150° with water and oxygen in a sealed tube for some hours consumes much of the oxygen with the formation of much mercuric acetate. Only a little metal separates, the confinement of its vapour checking the progress of dissociation.

Mercury perchlorates.

It is only necessary to refer to Chikashige's work on these salts in this laboratory (1895 ; this vol. p. 77) in which it is pointed out that a solution of mercurous perchlorate is obtained when the mercuric salt in solution is shaken with mercury.

Mercury oxalates.

Work upon the oxalates was unnecessary. It is known that mercurous oxalate heated to 100° changes partly into mercury and mercuric oxalate under the influence of its water of crystallisation.

The decomposition of mercurous carbonate is so intimately connected with that of the oxide, that it will be noticed in that connection.

Mercury chlorides.

Conversion of mercuric to mercurous chloride.—A cold solution of mercuric chloride, violently shaken in a bottle with large excess of mercury, quickly becomes deprived of all dissolved salt, in consequence of the conversion of the mercuric to mercurous chloride. Filtered thoroughly bright, the water gives only a faint browning with hydrogen sulphide. Such a simple way of removing mercuric chloride from solution may possibly find practical applications. The conversion, however, cannot be completed in the presence of much alkali chloride.

(*Literature and criticism*).—Gay-Lussac was aware that finely divided mercury acts freely upon a solution of mercuric chloride. It is also well known that when mercuric chloride and mercury are rubbed together with a little water or alcohol, as a first step in preparing calomel, much mercurous chloride is produced before heating. Yet in any edition of Gmelin's *Handbuch*, or in any other treatise, so far as I know, we find only that mercury and mercuric chloride form mercurous chloride *when heated together;* while among the *wet* ways of forming it, the direct union of mercury and mercuric chloride is not specifically given. Union in this way is not, indeed, well adapted to the preparation of mercurous chloride, but, as a mode of its formation,

is only second in scientific importance to the union of chlorine with mercury. To see given, as it is, a whole list of metals that convert mercuric chloride in solution into mercurous chloride, which includes silver but does not include mercury itself, is certainly strange.

Dissociation of mercurous chloride by heat.—The experiments made upon the dissociation of mercurous chloride were closely similar to those upon the nitrate. The mercurous chloride used had been precipitated by hydrochloric acid from the nitrate and well washed. One gram of it and 10cc. water heated seven hours in a flask immersed in boiling water, gave a sublimate of mercury in the condenser tube, a little of which rolled back into the flask. From first to last a gentle current of air was passing. The mercury found in solution as mercuric chloride was .0983 gram, and that collected from the condenser tube about .08 gram; the rest could not be collected. That the deficiency in the latter, or excess in the former, was incidental and not significant of oxidation, the next and some of the other experiments will show. A second experiment performed simultaneously with the last, and like it in everything except that a current of carbon dioxide was used in place of that of air, gave .1008 gram mercury in solution and about .08 gram sublimed in the tube. Again, an experiment was made in a current of air, but lasting eight hours and in which a little hydrochloric acid had been added to the water. This time, the mercuric radical was found to be .1307 gram, and the sublimed mercury secured, .1305 gram. The hydrochloric acid had seemingly increased slightly the extent of the dissociation. Two experiments were made, using dilute solution of potassium chloride instead of water. In one case, air was passed; in the other, carbon dioxide. The heating lasted six hours. In the air experiment, .1923 gram mercury was found in solution as mercuric chloride, and .1763 gram mercury as sublimate. In the carbon dioxide experiment, the

quantities were: .1823 gram in solution and .16 gram sublimed. The effect of the potassium chloride upon the dissociation had therefore been marked.

In all these experiments minute globules of mercury were visibly mixed with the mercurous chloride, thus accounting for the deficiency of sublimed mercury. The absence of oxygen in the carbon dioxide experiments showed that little if any oxidation could have occurred in the air experiments. Its absence may be assumed on the grounds of its absence in the nitrate experiments. In any case, dissociation of mercurous chloride in water at 100° is fully established by these experiments.

Of the dissociation of mercurous chloride by light I can say nothing, beyond referring to the fact that mercurous chloride turns dark brown in strong light.

Mercurous chloride not changed by boiling water except in slowly disappearing as mercury and mercuric chloride.—If shaded from daylight and contained in a porcelain or hard glass vessel, mercurous chloride may be boiled with distilled water, so long as any of it remains, without suffering any change in appearance or composition.

(*Literature and criticism*).—Very many statements of the results of experiments have been made, which, as admitted in Gmelin's summary of them, are often contradictory. Most of the work is so old that the original accounts of it could not be consulted; Gmelin-Watts' *Handbook* is the authority relied upon. Simon found mercurous chloride boiled with water in an open vessel to disappear very slowly, and in such a way that the still undissolved matter consists of unaltered mercurous chloride. Guibourt also stated that the residual mercurous chloride is unchanged. Simon and Guibourt's observations are therefore in agreement with mine. But the statements of Righini, Pagenstecher, Donovan, Gruner, Vogel, and Peschiar are to the effect that

mercurous chloride is rendered grey by boiling water, or by long boiling with water, and that it imparts mercury and chlorine to the water. Then, as to the greying, that is attributed to the formation of metallic mercury, or hypomercurous chloride, or oxymercurous chloride; while, as to the mercury going into solution, that is as mercuric chloride, or mercuric oxychloride, or both mercurous and mercuric chloride. In so far as these results, mostly obtained in connection with pharmacological studies, differ from those of Guibourt and Simon, and those here described, they may be attributed to the action of impurities derived from the exceedingly large proportions of water used, probably not always carefully distilled, and derived also from vessels of inferior glass and porcelain, or to the action of light, or to the heating having been carried out in long-necked flasks which allowed some of the volatilising mercury to condense and run down into the water.

The decomposition of mercurous chloride into mercuric chloride in presence of hot hydrochloric acid solution has long been well known; it was described by Proust and by Boullay early in the century. Pettenkofer, Pfaff, Hennel are early authorities for the also well known decomposition of mercurous chloride in presence of warm solutions of ammonium, sodium, and potassium chlorides. Of special interest are the grounds of belief that mercurous chloride and hydrochloric acid become mercuric chloride by the action of the air. Guibourt stated that all the mercurous chloride becomes mercuric chloride when it is boiled with water containing hydrochloric acid, and Fresenius (*Quantitative Analysis*) adopts this statement and gives an equation expressing aerial oxidation. As a fact, there is no evidence whatever, yet discovered, that any oxidation at that temperature takes place, while it is certain that dissociation is fully competent to account for all the facts observed. Positively must it be denied that more than

some relatively minute and unknown quantity of mercurous chloride becomes oxidised when it is boiled with water and hydrochloric acid till all has dissolved.

Closely connected with Guibourt's statement, there come in here interesting observations of Mialhé (1840–3), an account of which I take, with condensation, from Gmelin's *Handbook*. Agitated for an hour at 100° in a well closed bottle with a tenth of its weight of mercurous chloride, water takes up a thousandth part of the mercury as mercuric chloride, but if air has access to the liquid, more mercuric chloride is formed. In 24 hours, at 40–50°, in presence of hydrochloric acid, water takes up $^{7}/_{1000}$ of the mercury as mercuric chloride, when in a closed bottle ; but in the open air it takes up $^{23}/_{1000}$. In a closed vessel containing mercurous chloride with twice its weight of ammonium chloride and twice its weight of sodium chloride, and 33 times its weight of water, one hundredth of mercurous chloride dissolves as mercuric chloride in the course of 24 hours at 50° ; while in an open vessel 3.6 hundredths are dissolved. "Hence it appears that "more than two-thirds of the mercuric chloride is prodused by the "oxidising action of the air, and one-third by the decomposition of "calomel." No such assertion as this, as to oxidation being the cause of the observed phenomena, occurs in the Kraut-Jörgensen edition. The result of my experiments on this salt in this particular connection, which are given in the next paragraph, were feeble, but my other experiments upon it and those upon mercurous nitrate, already described, make it clear enough that Mialhé in his experiments got more mercuric chloride in an open vessel because then dissociation could proceed, whereas the retention of the mercury in the closed vessel stopped it. Confirmation of this statement will be found in the results of my experiments at 150° to be presently described. It is true that Mialhé ascertained that metallic mercury, unoxidisable as it is alone by

the air, does dissolve very slowly as mercuric chloride when it is exposed to the air under a layer of solution of an alkali chloride. But any such effect of the air upon the very small quantity of mercury liberated by dissociation from mercurous chloride in warm water must be utterly inappreciable.

Mercurous chloride not sensibly oxidised at lower temperatures.—I now describe a repetition of Mialhé's experiments with the crucial modification of using a current of carbon dioxide instead of one of air. Two flasks holding equal quantities of water and equal quantities of mercurous chloride were kept together at about 50° for 45 hours, the one flask containing air being closely corked, and the other fitted with reflux condenser and a tube through which a current of carbon dioxide was passing the whole time. The result was much more limited than that obtained when mercurous nitrate was operated upon, the mercuric chloride produced being exceedingly small in quantity. Had I used strong solutions of alkali chloride instead of water, no doubt the quantities of mercuric salt obtained would have been much larger and been measurable. But, as it is, my results here and from experiments upon the nitrate, entirely confirm Mialhé's, in so far as they show the production of much more mercuric salt in a current of gas than in a closed space. In the present experiment, the water from the flask through which carbon dioxide had been passing gave a marked blackening with hydrogen sulphide, while that which had been shut up with the mercurous chloride and air gave only a moderate browning. At the same time, they prove that in his experiments the exposure to the open air or to a current of air increased the production of mercuric chloride so largely, not by an oxidising action, but by carrying off mercury vapour, and thus favouring the progress of dissociation.

Oxidation of mercurous chloride at 150°.—While mercurous chloride

is not sensibly oxidised by the air at temperatures as high as 100° at least, it is readily oxidised at 150°. Heated for six hours with water, in an atmosphere of carbon dioxide in the tube, it underwent hardly any change, a very little mercury and mercuric chloride only being formed. Dissociation did not progress because of the retention of the mercury vapour. In other experiments I used, in one case, a 3.7 per cent. solution of hydrochloric acid instead of water merely, and in another case, a 6.5 per cent. solution of potassium chloride. Here the presence of the acid or of the potassium chloride caused a small amount of dissociation into mercury and mercuric salt, showing that at this temperature, mercurous chloride approaches the iodide in its readiness to drop mercury in presence of the potassium salt. Very different were the results when the air of the tube had been displaced by oxygen before sealing. There was still only very little metallic mercury observed, but there was now much mercuric salt obtained. When water alone was used and the heating had lasted six hours, the mercuric chloride was found partly in solution, and partly as brilliant micaceous scales, brown in colour, of oxychloride. When the water contained hydrochloric acid in one case and potassium chloride in another case, in the proportions given above, all the mercuric salt was found in the solution. In all cases there had been large absorption of the oxygen. In presence of hydrochloric acid, so mnch as 47.5 per cent. of the mercurous chloride (one gram) became mercuric chloride; in the potassium chloride solution the conversion was much less though still considerable, it having extended to 19 per cent. of the mercurous chloride. In this case, too, the solution was very alkaline. In another experiment where 50cc of the 3.7 per cent. hydrochloric acid were taken and the time of heating was extended to ten hours, even 60 per cent. of the mercurous chloride (one gram) changed into mercuric chloride. The superior efficiency of hydrochloric acid over potas-

sium chloride in promoting oxidation is even greater than the numbers make it appear, for, in the potassium chloride experiment, there was more dissociation, as shown by the greater separation of metallic mercury.

Mercury bromides and iodides.

No new experiments upon the bromides and iodides seemed called for, it having been ascertained by others that mercurous bromide dissociates in hot solutions of alkali bromides, while every one knows how readily mercurous iodide decomposes in solution of potassium iodide, and is formed by rubbing mercury and mercuric iodide together.

Mercurous oxide and carbonate.

That mercurous oxide, or what passes for it, decomposes more or less at the common temperature into mercuric oxide and mercury has long been generally known, but it remained for Barfoed in 1883 to prove beyond question, that the black substance produced by the action of alkalis upon mercurous salts is really something more than a mixture of mercury and mercuric oxide. From almost the first moment of its production it contains metallic mercury and, therefore, mercuric oxide, but that it is, at first, real mercurous oxide, for the most part, Barfoed has established very conclusively by two of its properties. Its specific gravity in the fresh state is 11.13, while that calculated for mercury and freshly precipitated mercuric oxide in the required proportions is 12.14. Secondly, the substance is oxidisable in the air, while mercury, even finely divided, is not so. When exposed to the air long enough all its metallic mercury volatilises, mercurous oxide also disappears, and nothing but mercuric oxide remains. In this change, the mercurous oxide continues, no doubt, to decompose into mercury and mercuric oxide, but much of it certainly

oxidises in the air. In a closed space, in presence of air, it increases in weight, for there is then no appreciable loss due to volatilisation of mercury, while there is combination with oxygen. But exposed to the open air in thin layers there is loss in weight, because then the effect of volatilisation of mercury more than counterbalances that of taking up oxygen. In a closed space the substance never becomes yellow, because the mercury cannot volatilise. That oxidation always goes on in air till finished is also shown by the fact that the residual mercuric oxide weighs much more than 52 per cent. of the original substance. Bruns and von der Pfordten (1888) have also observed that mercurous oxide oxidises in the air and that the presence of moisture in the air hastens the oxidation. I myself made a number of experiments before I had read Barfoed's paper in full. A summary statement of all the results will be of interest.

Barfoed by exposing .523 gram for a month in a bell jar standing over water observed an increase of weight equivalent to .067 per cent. *per diem*. That represents the oxygen taken up under very favourable conditions and no material loss of mercury.

Bruns and von der Pfordten exposed 5.7635 grams to the air for 12 hours only and observed an increase of weight equal to .32 per cent. *per diem* (24 hours). This represents the difference of the gain in oxygen and loss in mercury. The same chemists exposed 10.8543 grams in a desiccator for 48 hours, and observed an increase equal to .085 per cent. *per diem*, an increase somewhat larger than Barfoed got as the average increase a day, during a month in moist air. In this experiment there will have been no material loss of mercury.

I exposed, in cold dry weather, in an open porcelain crucible for 15 days, 5.1037 gram, weighing every two days about. The average increase in weight *per diem* was .025 per cent., and the rate of increase, though not very regular, was

not less near the end of the exposure than on the first days.

I exposed in cold, dry weather, in a crusible for 17 days, 6.9874 grams. This time the rate of increase varied but little from first to last, and was equal to .023 per cent. *per diem.* In this and the previous experiment the result represented the joint effect of gain of oxygen and loss of mercury.

I spread moist over a glass dish, what when dry weighed .840 gram. In a desiccator, it decreased in weight, but only .001 per cent. in 13 days, which seems to prove that mercurous oxide does not oxidise in dry air. The same portion was then exposed to cold dry air for 14 days, during which time it lost in weight at the rate of .004 per cent. *per diem*, as the combined result of loss of mercury and gain of oxygen. The oxidation of mercurous oxide is, therefore, a very slow process. So far as can be ascertained, this oxide is the only mercury compound that does oxidise at the common temperature, or even at 100°.

Mercurous carbonate is formed when moist mercurous oxide is exposed to carbon dioxide gas (Barfoed). In the air, it slowly decomposes into carbon dioxide, mercury, and mercuric oxide.

Non-existence of mercurous sulphide.

When a solution of mercurous nitrate is added to one of potassium cyanide, it is well known to produce a precipitate of half its mercury as metal and to form mercuric potassium cyanide in solution. When mercurous nitrate is added to excess of hydrogen sulphide, it is represented by nearly all English authorities (I do not know an exception) to yield mercurous sulphide which begins at once to decompose and, therefore, becomes a mixture of mercurous and mercuric sulphides with metallic mercury. Yet, so long back as 1863, Barfoed submitted satisfactory proof that hydrogen sulphide behaves like potassium cyanide in at once converting a mercurous salt into mercury and mercuric sulphide, and, therefore, that mercurous sulphide has no more

existence than mercurous cyanide. Continental writers, generally, have accepted Barfoed's results and state that mercurous sulphide is unknown. Examples may be seen in the English translations of Fresenius and Menschutkin. Kraut-Jörgensen's *Gmelin* adopts Barfoed's account of the matter.

The argument in disproof of the existence of mercurous sulphide is essentially that the precipitate caused by hydrogen sulphide in mercurous nitrate has not been shown to differ in any property from a mixture of mercuric sulphide and mercury. In some attempts to make a quantitative separation of the mercury and mercuric sulphide, I got some results which seem worth recording. When the black precipitate is digested with cold nitric acid, even only strong enough just to act upon it, it quickly begins to whiten, in consequence of being converted into mercuric-sulphide-nitrate. To try to avoid this result, some of the fresh precipitate, washed and moist, was treated, on a filter of SS hardened paper, five times with small quantities of nitric acid, sp. gr. 1.2, the acid being drawn through as quickly as possible by a filter pump. The last portion of acid went through free from mercury and the precipitate had preserved its black colour ; but the mercury which had been dissolved out by the nitric acid did not reach to a half but only 40 per cent. of the whole. The precipitate was, therefore, washed free from nitric acid and then stirred up with hydrogen sulphide-water, which extracted nitric acid from it, and thus showed that, though not changed in colour, it had yet come to contain some combined mercuric nitrate. Complete separation of the mercury from the mercuric sulphide by nitric acid seems therefore not to be practicable. The nitrous acid formed in the dissolution of the mercury is no doubt the active agent in causing some of the mercurous nitrate to become mercuric nitrate in contact with mercuric sulphide.

The fresh black precipitate, I found to be quickly acted upon by

a solution of mercuric nitrate, and the products to be mercurous nitrate and mercuric sulphide nitrate. Probably, too, there is a quantitative separation effected of the metallic mercury and the mercuric sulphide. But, even so, this would not in itself be a proof of the matter in question, because mercurous sulphide might well by double decomposition with mercuric nitrate become mercuric sulphate and mercurous nitrate, and then the former unite with more mercuric nitrate. Notwithstanding that the two components of the mixture cannot be quantitatively separated, the fact remains that mercury and mercuric sulphide behave together just as does the supposed mercurous sulphide. Thus, cold nitric acid, sp. gr. 1.2, does not by itself convert precipitated mercuric sulphide into the white sulphide-nitrate, but does so if some mercury is present. It is known too, that mercuric sulphide is whitened by digestion with a solution of mercuric nitrate.

In conclusion I wish to record gratefully my indebtedness to Dr. Edward Divers, F.R.S. for his guidance in carrying out this research, and for the large part he took in putting the account of it together.

Imidosulphonates.

(Second paper)

by

Edward Divers, M.D., F.R.S., Prof.

and

Tamemasa Haga, F.C.S., *Rigakuhakushi,* **late Asst. Prof.,**

College of Science, Imperial University.

This communication is supplementary to that which appeared in this *Journal*, vol. 6, in 1893. It contains an account of some imidosulphonates, not there described, and a collation of our results with those obtained by Berglund, called for by the existence of some radical differences between them. It was this chemist, now deceased, who first made known the existence of imidosulphonates, although several of them had been already obtained and described by others under various names and formulæ. His important memoir on these salts was published in Swedish, but summaries of it by Clève and by himself, respectively, appeared in the Journals of the French and German Chemical Societies. References to all are given in our first paper. In English also a good summary was published by Watts in the *2nd. Suppl.* of his *Dictionary*. This had escaped our notice and up to the time of publishing our first paper we had only seen the account in the *Berichte* and an appreciative notice of the Swedish paper in Raschig's paper on Fremy's sulphazotised salts. But soon after that, Dr. Raschig spontaneously sent us, with the greatest kindness, his own copies of Berglund's Swedish papers on *Imidosulphonates*

and *Amidosulphonates.* A perusal of these led us to resume work on the subject with the intention only of examining into the differences between his results and ours, but we went further afield and prepared a few new salts, because they promised to be of interest.

For convenience of reference, we follow in this paper the order of description observed in the former paper and reproduce, as briefly as possible, matters of interest in Berglund's paper in Swedish not to be found in chemical literature outside it. A full list of the salts prepared by him is given by Watts (*op. cit.*)

Berglund's first source of imidosulphonates was ammonia and chlorosulphonic acid, but afterwards he had resort to potassium nitrite and sulphite, following Fremy, with modifications which do not call for notice here.

Alkali imidosulphonates.

Ammonium imidosulphonates—Berglund failed to get normal ammonium imidosulphonate ; the statement in Watts' *Dictionary* that he did get it is therefore erroneous. He believed Rose's 'vitreous sulphatammon' to be this salt, but our own experience has convinced us that this substance, before as well as after its crystallisation from water, is the two-thirds normal imidosulphonate, and that Rose's 'flocculent sulphatammon,' not noticed by Berglund, is indeed anhydrous normal ammonium imidosulphonate. To Woronin is due the accurate distinction between the two salts.

The mother-liquor of the crystals of the two-thirds normal ammonium imidosulphonate ('parasulphatammon') gave Rose on evaporation his so-called 'deliquescent salt.' This Berglund considered, it appears from his later paper on *Amidosulphonic acid*, to have been a mixture of amidosulphonate and the two-thirds normal imidosulphonate with ammonium acid sulphate.

Sodium imidosulphonates.—That, contrary to Fremy's experience, sodium nitrite can be sulphonated as easily as potassium nitrite was ascertained by Raschig and by us about the same time, and later we ourselves prepared the normal and two-thirds normal sodium salts, as well as some compound salts. Berglund, however, had prepared the normal sodium salt and also the mercury sodium salt, but not by sulphonating sodium nitrite. He either boiled ammonium imidosulphonate with sodium hydroxide till all ammonia had been expelled, or, more satisfactorily, he precipitated by potassium chloride the two-thirds normal potassium salt from the ammonium salt; dissolved it in a boiling solution of sodium hydroxide and chloride; and then by cooling crystallised out the normal sodium salt. His description of the normal sodium salt, so far as it goes, agrees with ours. The crystalline salt which he sometimes got in place of the ordinary normal sodium salt, and which he believed to be that salt in the anhydrous state, we take to have been a double salt of normal sodium imidosulphonate and potassium chloride.

He did not obtain the two-thirds normal sodium imidosulphonate, nor its compounds with ammonium nitrate and with potassium nitrate, nor sodium ammonium imidosulphonate.

Barium imidosulphonates.

Berglund's account of *normal barium imidosulphonate* agrees with ours, even to the detail that, like us, he once got it pure by a first precipitation, but in all other instances found it necessary to free the first precipitate from potassium or sodium, as the case might be, by dissolving it in hydrochloric acid and reprecipitating it with baryta (or barium chloride and ammonia). He was really the first to prepare this salt and did himself injustice in crediting Woronin and Jacquelain with its previous preparation. Woronin never analysed his product,

which was almost certainly a double salt. Jacquelain did very completely and carefully analyse his, and the result shows it to have been a barium ammonium salt, as we explained in our first paper. Berglund found the normal barium salt to give up its 5 mols. of water almost completely at 100° ; we maintain the accuracy of our statement that it loses water only very slowly even at 115° (see further on this point our account of the strontium salt). Barium imidosulphonate is soluble in a solution of ammonium chloride.

Two-thirds normal barium imidosulphonate was fully described by Berglund, his account agreeing with ours.

Double salts of barium with alkalis received peculiar treatment by Berglund. He did not formally recognise their existence and relegated to foot-notes observations which, he admitted, made their existence probable. He could not satisfactorily formulate the composition he found them to have, and for him they remained as impure barium salt only. Yet our own work confirms the results of his and makes it possible to give formulæ to his preparations. First, there is $Ba_{12}K_8H(NS_2O_6)_{11}$, $11H_2O$, which he constantly obtained when he added normal potassium imidosulphonate to barium chloride. Had he thought of the device, here adopted, of introducing the atom of hydrogen into the formula, he would probably have not looked upon his analytical results as incapable of being interpreted. A sodium salt described by us, comes very near to this salt, being $Ba_{11}Na_8(NS_2O_6)_{10}$, $13H_2O$; for if we subtract a mol. of the two-thirds normal barium salt, $BaHNS_2O_6$, from his formula and write Na for K, we get ours. Evidently, either salt is mainly $BaK(\text{or } Na)NS_2O_6$ with a little $Ba_3(NS_2O_6)_2$. By adding two-thirds normal potassium salt to ammonia and barium chloride, he got $Ba_{12}K_7(NH_4)_2(NS_2O_6)_{11}$, $79H_2O$. Lastly, the salts, $Ba_6(NH_4)_2H(NS_2O_6)_5$, $21H_2O$ and $Ba_7(NH_4)(NS_2O_6)_5$, $22H_2O$; all three having an obvious relation to the first. We have described a

still more ammoniated salt, $Ba_5(NH_4)_2(NS_2O_6)_4$, $8H_2O$. All these double salts of barium are granular and powdery, and quite unlike the peculiarly soft, clinging, pure barium salt.

Strontium imidosulphonates.

According to Berglund, normal strontium and normal calcium imidosulphonates are in properties, water of crystallisation, and conditions of formation, as like each other as two salts can be, but unlike the normal barium salt. This account of the normal salts puzzled us, but when we found his description of the properties and way of preparation of the calcium salt applies perfectly, so far as it goes, to a salt, described by us in our first paper, which we had found to be calcium sodium imidosulphonate, we lost all confidence as to the accuracy of his account. We therefore studied the strontium salts for ourselves, having omitted to do so before, when preparing our first paper.

Normal strontium imidosulphonate, according to Berglund, gradually separates in acicular prisms when a solution of strontium chloride, moderately concentrated, is mixed with one of either normal sodium imidosulphonate, or of diammonium imidosulphonate to which ammonia has been added. Its composition is expressed by $Sr_3(NS_2O_6)_2$, $6H_2O$, and it loses by heat, even at 130°—140°, only two-thirds of its water. In preparing it, it is unnecessary, he said, to take any care to have the strontium chloride in excess, although it is very important to keep the barium chloride in excess when preparing the normal barium imidosulphonate.

Normal strontium imidosulphonate, according to our experience, cannot be obtained by mixing together strontium chloride and normal sodium imidosulphonate, but always strontium sodium imidosulphonate. But from this salt it can be obtained just in the same way as

the normal barium salt is prepared from the barium potassium or barium sodium salt, namely, by dissolving the strontium sodium salt in dilute hydrochloric acid and pouring the solution at once into slight excess of a warm concentrated solution of strontium hydroxide, and repeating the operation twice, or until all sodium has been removed. So long as the re-precipitated salt contains sodium, it is a hard granular precipitate, but when it is free from sodium, it separates as glistening, thin, scaly crystals, which felt together into soft voluminous flocks, which, dried on the tile, form coherent flakes retaining water in their interstices with great obstinacy, like the barium salt, to which it has indeed much resemblance. It is more soluble in water than the barium salt, and is actually soluble in hot water to a considerable extent. For analysis we comminuted its flaky mass and pressed the particles between filter paper till it seemed quite dry. But on exposure to air for days such a preparation continuously loses water and much of it before the crystalline lustre sensibly diminishes.

The freshly dried salt contains 12 mols. water, as the following numbers show :—

	Calc.	Found.
Strontium,	31.75	31.86
Sulphur,	15.51	15.49
Water,	26.13	—

Tested after 14 days exposure, the water amounted to only 7 mols. although efflorescence had only then just become apparent. The strontium was then 35.61 per cent., while calculation for 7 mols. water gives 35.66 per cent.

By decomposing the normal hydroxy-lead imidosulphonate with ammonium hydrogen carbonate, so as to obtain a weak solution of normal ammonium imidosulphonate, and then evaporating to a small

volume, we obtained a concentrated solution of the two-thirds normal ammonium salt, the strength of which we determined by analysis. To it we added enough ammonia to make it a little more alkaline than the normal salt. It was then mixed with a slight excess of concentrated solution of strontium chloride and left to stand. Only a very small quantity of precipitate formed and this remained for the most part suspended in the solution. We therefore added excess of somewhat concentrated ammonia water which greatly increased the quantity of the precipitate, but the whole had such an unpromising appearance that we did not care to try to separate the salt for analysis, probably a strontium ammonium salt. We placed the whole in a desiccator over anhydrous potassium carbonate and left it there until it had nearly evaporated to dryness. We now added water which left a white opaque powder, the mother liquor smelling mildly of ammonia. Analysis of the powder proved it to be normal strontium imidosulphonate, with a slight quantity of ammonia in addition. Our calculation is for a pure strontium salt with 5½ mols. water. The salt may, however, be regarded as having only 5 mols. water. We determined the alkalinity of the salt and have expressed it as strontium, thus showing it to be more than a third of the total strontium. The excess of base may be regarded as consisting of ammonium, the presence of a little of which was established.

	Calc.	Found.
Strontium,	37.00	37.01
Alkalinity as strontium,	12.33	12.66
Sulphur,	18.04	17.98

When a solution of the normal strontium salt with 12 mols. of water is boiled, precipitation of sandy particles occurs. The

precipitate is nearly insoluble. It is a slightly basic* strontium salt, with about 5 mols. water. The calculation given is for normal strontium imidosulphonate with 5 mols. water.

	Calc.	Found.
Strontium,	37.47	39.02
Sulphur,	18.27	18.36

An opaque, powdery salt is also precipitated when the mixed solutions of strontium chloride and normal ammonium imidosulphonate are boiled. It contains a very little ammonia and is no doubt a slightly basic ammoniacal strontium salt. We have not quantitatively analysed it.

We have not attempted to prepare the *two-thirds normal strontium salt*, though it could no doubt be easily got, like the calcium salt (p. 204). Berglund prepared a solution of it, but found the salt so soluble and so difficult to crystallise that he did not work further upon it.

Strontium sodium imidosulphonate is obtained when solutions of normal sodium imidosulphonate and strontium chloride are mixed. Probably, the proportions taken matter little. We have used 2 mols. of the imidosulphonate to 3 mols. of the strontium salt in moderately concentrated solutions. When mixed, precipitation occurs but the precipitate redissolves on shaking and soon small prisms of the strontium sodium salt separate. The salt is sparingly soluble and resembles the calcium sodium salt, described in our first paper. Like that salt, too, it contains 3 mols. of water, its formula being $SrNaNS_2O_6$, $3H_2O$.

* We have got results indicating the existence of a hemihydroxy salt, $(HOSr)_3NS_2O_6$, corresponding with the lead salt, but have not had time to establish the fact.

	Calc.	Found.	
Strontium,	25.84	25.96	25.97
Sodium.	6.81	—	6.69
Sulphur,	18.93	18.89	—
Water,	15.95	—	—

Berglund got granular precipitates of a *strontium potassium salt* soon after mixing normal potassium imidosulphonate solution with strontium chloride solution. Calculating from his results, we find the salt was represented by the formula $Sr_{12}K_8H(NS_2O_6)_{11}$, $13H_2O$, in close agreement with the composition of his barium potassium precipitates, as calculated by us.

Calcium imidosulphonates.

By mixing solutions of normal sodium imidosulphonate and of calcium chloride, Berglund got what he described as the normal calcium salt, while, by proceeding in the same way, we have never got but the calcium sodium salt described in our first paper. Berglund's salt and ours agree in the descriptions given of them by him and us respectively, and they would have the same composition, if for the atom of sodium in our salt we put half an atom of calcium. Now Berglund estimated the calcium from the weight of the residue left by the ignited salt, and so little difference would there be in the weight of the residue by the presence of sodium in place of a third of the calcium, that the percentage numbers would only vary within the limits of error of an ordinary analysis. Possibly, therefore, he mistook the mixed sulphates for pure calcium sulphate, but whether that was the case or not, his normal calcium salt is like our calcium sodium salt and unlike our normal calcium salt, which we describe for the first time.

Normal calcium imidosulphonate.—The true normal salt can be prepared by stirring together the insoluble normal silver salt with its equivalent of calcium chloride in solution, decanting from silver chloride, and evaporating the solution in a desiccator till the new salt crystallises out. It is only sparingly soluble in water, when once separated from solution, and forms rectangular prisms and tables, stable in the air. It is strongly alkaline to litmus. Its composition is expressed by $Ca_3(NS_2O_6)_2.\ 8H_2O$.

	Calc.	Found.
Calcium,	19.60	19.60
Sulphur,	20.92	21.06

Berglund states that the normal calcium salt is also got from a mixed solution of ammonium imidosulphonate, ammonia, and calcium chloride. This mixture gives us no insoluble salt.

Two-thirds normal calcium imidosulphonate.—This salt is obtained by decomposing normal silver imidosulphonate by two-thirds of its equivalent of calcium chloride and one-third of its equivalent, or for safety just a very little less, of hydrochloric acid. The solution, separated from silver chloride and evaporated in a desiccator very far, becomes a mass of radiating prisms. Crushed and drained dry, the salt is permanent in the air, at least for days. Its reaction is slightly acid to litmus. Its formula is $CaHNS_2O_6,\ 3H_2O$.

	Calc.	Found.
Calcium,	14.87	14.70
Sulphur,	23.79	23.59

Calcium sodium imidosulphonate, $CaNaNS_2O_6,\ 3H_2O$, is described in our first paper, and has been referred to on p. 203, as being what we get by following Berglund's directions for preparing his normal calcium salt. The *mercury calcium salt* will be found described on p. 211.

Lead imidosulphonates.

We have indicated the existence of an unstable salt, $PbHNS_2O_6$, in solution, and Berglund has done the same.

The crystalline, normal hydroxy-lead imidosulphonate, described by us, $(HOPb)_3NS_2O_6$, has also been described by him, and our accounts agree. But his way of preparing it was to add ammonia gradually to mixed solutions of diammonium imidosulphonate and lead acetate so long as the amorphous precipitate it at once produces gives place to a crystalline one. When the last-formed amorphous precipitate does not disappear, addition of ammonia is exchanged for that of acetic acid until it has just been converted to the crystalline precipitate.

The amorphous precipitate obtained by the use of ammonia in excess and by using basic lead acetate he found to be a basic compound of varying composition. It is the lead salt which Jacquelain seems to have used for the isolation of imidosulphonic acid. We have shown in our first paper (**6**, 90) that a basic lead imidosulphonate can be uniformly obtained of the composition, $(HO)_5Pb_4NS_2O_6$.

Silver imidosulphonates.

Berglund has described only the normal silver salt. We have described this and two other, crystalline, well-characterised salts, $Ag_2NaNS_2O_6$ and $AgNa_2NS_2O_6$, the latter obtained when silver nitrate is added to excess of normal sodium imidosulphonate, circumstances in which, according to Berglund, a precipitate forms that is richer in silver than the normal argentic salt. This apparently strange result is explicable through the fact that he worked with highly dilute solutions, for as we have pointed out (**6**, 95), the salt $AgNa_2NS_2O_6$ is partly

decomposed by much water into silver oxide and two-thirds normal sodium imidosulphonate.

Mercury imidosulphonates.

Oxymercuric hydrogen imidosulphonate, $HN(SO_3HgO)_2Hg$, (Divers and Haga); *normal oxymercuric imidosulphonate*, $Hg[N(SO_3Hg)_2O]_2$, (Berglund).—Berglund and we have each described a basic mercuric imidosulphonate, ours differing from his in having $S_4 : Hg_6$ instead of $S_4 : Hg_5$. He prepared his salt from mercury potassium imidosulphonate and mercuric nitrate, and we ours from normal sodium imidosulphonate and mercuric nitrate. They ought therefore to have been the same. Berglund tried the use of normal potassium imidosulphonate and thus got a more basic product, but this he attributed to the presence of mercuric oxide or basic nitrate in the precipitate. In agreement with this, one might account for our getting a more basic salt than his. Or, conversely, one might account for his getting a less basic salt than ours, by accepting that some of the very little soluble two-thirds normal potassium imidosulphonate precipitated along with the mercury salt, thus raising the quantity of sulphur and lowering that of mercury. There was also the possibility of unconscious bias on his part or on ours leading to a selection of those results as more reliable which were capable of being expressed according to our particular preconceptions. For Berglund was strongly impressed by the tendency of mercury to displace the imidic hydrogen, while we were similarly struck with the fact that whenever sulphuryl occurs in combination with oxylic mercury in a precipitated salt, that mercury functions as the bivalent radical $-HgOHgOHg-$; and it will be seen, on referring to the formulæ in the heading of this paragraph, that Berglund's ratio of sulphur to mercury accords with his preconception and not with ours, and that our ratio accords with our preconception and not with his.

However, while he had two products to select from, we must now say that we had not, and still have not, always getting one and the same basic mercuric salt.

To make sure that we had not been mistaken, and therefore that Berglund's finding could not be confirmed, we have made further experiments,—in one of them following him as closely as possible, in others striving by means of more acid solutions to reduce the basicity of our precipitates to that of his. But, before stating these experiments and their results, we have two adverse comments to make upon those reported by Berglund.

One is as to the precipitation of mercuric oxide or basic nitrate inferred by him. However prepared, our product has always been one of the whitest of precipitates, only assuming a faint buff tint when kept for some time at 100° or higher in the dry state. The presence of very little oxide or basic nitrate should have shown itself by a yellowish colour. No precipitate we have tested of the present salt, of the oxymercuric sodium salt (**6**, 105), of the mercurous salt (this paper, p. 212), or of the mercurosic salts (this paper, p. 214), has ever shown the presence of nitric acid in it. Nor can Berglund's supposition, that mercuric oxide or basic nitrate might be precipitated, be adopted as probable, when it is considered that the mother-liquor of the precipitating salt is much more strongly acid than the solution of mercuric nitrate used.

The other matter to be pointed out is the unlikelihood of mercury taking or retaining the imidic relation in a salt precipitating from such very acid mother-liquors ; since, as we have shown in our first paper, dilute nitric acid replaces such mercury by hydrogen. Berglund thought this not to be the case, but it is so nevertheless. Now, directly the attempt is made to lessen the quantity of nitric acid enough to let mercury take the imidic relation, sodium or potassium also

enters the salt, displacing half the oxylic mercury. For we then find that we pass abruptly from $HN(SO_3HgO)_2Hg$ to $Hg\begin{cases} N(SO_3HgO)_2Hg \\ N(SO_3Na)_2 \end{cases}$.

Exp. I—To excess of very dilute mercuric nitrate (necessarily acid) was added a very dilute solution (1 in 50) of mercury sodium imidosulphonate. Almost at once precipitation began, first as a diffused opacity, soon as a dense crystalloidal deposit, leaving the solution quite bright. The precipitate, washed by decantation with much water, was dried on a tile. It and its fresh mother-liquor were free from sulphate. Composition:—mercury, 73.70 %; sulphur, 7.98 %; sodium 0.08 %.

Exp. II.—Mercuric nitrate solution, 250ccs, containing, 6 grams mercuric oxide which had been dissolved in nitric acid one-sixth more in quantity than that equivalent to it; 250ccs. of a solution containing 4 grams of mercury sodium imidosulphonate: these solutions mixed very soon gave a soft, voluminous, crystalline precipitate which readily settled. After decanting its mother-liquor, it was washed once with dilute nitric acid and then with water repeatedly. Drained dry on a tile, it weighed 6½ grams, or four-fifths of the calculated quantity. It was free from sulphate, as was also its mother-liquor. Composition:—mercury, 73.44 %; sulphur, 7.94 %; sodium 0.08 %.

Exp. III.—Dissolved 2.8 grams mercury potassium imidosulphonate in 250ccs. water, and added it to 3 grams of concentrated mercuric nitrate solution containing almost 1.5 grams of mercury as nitrate. A crystalline precipitate at once formed; after a few moments active stirring, the precipitate was allowed to settle and the bright mother-liquor was decanted into another vessel containing 4.5 grams more of the mercuric nitrate solution. A second precipitate was thus obtained: both were washed by decantation and drained on tiles. The first weighed 2 grams; the second 1.5 grams: by calculation each

would have weighed 2.9 grams, had none remained dissolved, according to the equations,—

1. $HgN_2(SO_3)_4K_4 + 2Hg(NO_3)_2 + 2H_2O$
$= HN(SO_3)_2Hg_3O_2 + 2KNO_3 + 2HNO_3 + HN(SO_3)_2K_2$;

2. $HN(SO_3)_2K_2 + 3Hg(NO_3)_2 + 2H_2O = HN(SO_3)_2Hg_3O_2 + 2KNO_3 + 4HNO_3$.

The first precipitate contained—mercury, 72.85%; sulphur, 8.03%; potassium, 0.3%; the second contained—mercury, 72.61%; sulphur, 8.11%; potassium, 0.38%. From which it is seen that in no case is alkali metal absent; that the quantity present is markedly greater in the case of potassium than in that of sodium; and that the potassium is a little more in quantity in the presence of more nitric acid (the same was found true of sodium in the earlier experiments. This apparently strange result is quite natural, for nitric acid dissolves mercuric imidosulphonate, without having any action upon the two-thirds normal potassium or sodium salt.

The results of the above experiments, together with those described in our first paper, can, we think, leave no doubt that the basic mercuric salt has the composition, $HN(SO_3HgO)_2Hg$, the percentage numbers for which are—mercury, 74.35; sulphur, 7.93. For, the potassium present in the precipitates of *Exp. III* above, fully accounts for the slight deficiency of the mercury in them. As already stated, it is probable that Berglund got his analytical results as a consequence of the presence of unobserved potassium.

Mercury ammonium imidosulphonate.—From the mercury calcium salt, described on p. 211, we tried to prepare the mercury ammonium salt by decomposing it with just enough ammonium acid carbonate. Success seemed to follow, but in a very few minutes a secondary decomposition set in. That is to say, at first calcium carbonate alone precipitated with effervescence of carbon dioxide, which

was the normal effect; but, after stirring well till the effervescence had subsided, the solution began again to effervesce and to deposit a basic mercuric calcium salt, possibly analogous to the sodium salt and therefore, $Hg\begin{cases} N(SO_3HgO)_2Hg \\ N(SO_3)_2Ca \end{cases}$.

When the effervescence had again subsided, the precipitate and mother-liquor proved to be—the one, a mixture of calcium carbonate and basic mercury calcium imidosulphonate, roughly separable by dilute nitric acid; the other a solution of normal and two-thirds normal ammonium imidosulphonate, with a very little mercury calcium imidosulphonate, or the equivalent of these salts. No amidated mercury salt was produced.

Berglund also tried to make the mercury ammonium salt, but without success, from the mercury barium salt and ammonium sulphate. In this case, too, almost all the mercury was precipitated as basic salt, and ammonium imidosulphonate left in solution. The salt appears to be, therefore, incapable of continued existence.

Mercury potassium imidosulphonate.—According to Berglund, dilute nitric acid has no action upon this salt, but, as we have pointed out, the acid converts it into the insoluble two-thirds normal potassium salt and mercuric nitrate.

Mercury sodium imidosulphonate.—This salt was described by us fully, under the belief that Berglund had not prepared it, in which we were mistaken. We prepared it from mercuric nitrate with facility, while he used the chloride, having found the nitrate to give a product containing no sodium, probably because his solution was too acid or added too freely. We found the water of crystallisation to be about $5\frac{1}{2}$ atoms and gave it as 6 atoms. Berglund found 5 atoms of water. We have again prepared and examined the salt, and have now got results in excellent agreement with $5H_2O$. Therefore, his formula

is right, $HgN_2(SO_3)_4Na_4,5H_2O$. We have also found now that the salt, left in a vacuum over sulphuric acid for weeks, loses all its water, and not merely two-thirds of it, as stated in our first paper. Berglund dried his salt at 100°.

Oxymercuric sodium imidosulphonate.—No knowledge of such a salt as the basic mercury sodium salt, which we have described in our first paper, was possessed by Berglund, or of a corresponding potassium salt. But it is interesting to find that he could not get the mercury silver salt, but only a mercury silver potassium salt, by mixing normal mercury potassium imidosulphonate with silver nitrate even in excess. His formula for this salt, $Hg\begin{cases}N(SO_3Ag)_2\\N(SO_3K)_2\end{cases}, 3H_2O$, is quite analogous to ours for the basic mercury sodium salt, $Hg\begin{cases}N(SO_3HgO)_2Hg\\N(SO_3Na)_2\end{cases}, 3H_2O$. The water of crystallisation in this mercury salt was found by us to be too low for the $4H_2O$ adopted by us, and we would now write it $3H_2O$, which agrees slightly better with the results of analysis.

Mercury calcium imidosulphonate.—Berglund obtained and described mercury barium, mercury strontium, and mercury magnesium imidosulphonates, but failed to get the mercury calcium salt, because of its free solubility in water. We have prepared it by dissolving mercuric oxide in a warm solution of two-thirds normal calcium imidosulphonate, filtering, evaporating, crystallising, and, finally, recrystallising from water. It forms small brilliant prisms.

	Calc.	Found.
Mercury,	25.90	25.92
Calcium,	10.36	10.20
Sulphur,	16.58	16.61

A compound of this salt with mercuric chloride, which can be formulated as $ClHg_2(NS_2O_6Ca)_3$, $12H_2O$, and, therefore, be compared with

apatite, was got in small good crystals by treating oxymercuric hydrogen imidosulphonate with calcium chloride solution, in the proportion, $HNS_2O_6Hg_3O_2 : CaCl_2$. Much mercuric oxychloride remained insoluble, and the solution evaporated in a desiccator gave the salt in question. By dissolving in water and precipitating by absolute alcohol, the mercuric chloride can, for the most part, be removed from the mercury calcium imidosulphonate, but only with great loss of the latter, in consequence of its own solubility in alcohol.

	Calc.	Found.
Mercury,	30.92	31.00
Calcium,	9.28	9.35
Sulphur,	14.84	14.55
Chlorine,	2.74	2.63

Mercurous imidosulphonate.—No mercurous imidosulphonate has yet been described. There seems to be only one, a basic salt, which is formed when two-thirds normal sodium imidosulphonate is added to mercurous nitrate. Being a basic salt, having $Hg_4 : S_2$ its formation is accompanied by that of nitric acid, which again, is a solvent of it ; so that under the most favourable conditions a third, at least, of the imidosulphonate remains in solution. The normal sodium imidosulphonate would, therefore, be preferable to use, were its use not subject to a disturbing effect, to be noticed presently. In order to limit the quantity of nitric acid, the normal mercurous nitrate, in powder, is stirred with hot water until it has all become a solution, holding in suspension a little of the soft, voluminous basic nitrate, and free from any yellow granular particles. It has to be in some excess, and we have taken about one-fifth more than the calculated quantity ; but with moderate excess only, there will be no liability of any basic

nitrate remaining insoluble, because of the nitric acid which is generated. The equation expressing the reaction is—

$$(4HgNO_3)_2 + H_2O + 2HN(SO_3Na)_2 = O[Hg_4N(SO_3)_2]_2 + 4NaNO_3 + 4HNO_3.$$

Of the sodium salt 1.05 grams, dissolved in about 150 ccs. water, added with stirring gradually to 4.5 grams mercurous nitrate in about 20 ccs. water, gave a precipitate weighing 2.75 grams, and nitric acid in solution weighing 0.33 gram, the ratio of these weights being in accordance with the above equation. The precipitate was tested for nitrate and sulphate, and none found; and the nitric acid in solution was measured by titration with sodium hydroxide, after addition of excess of sodium chloride had been made. The mother-liquor contained no sulphuric acid.

The new salt is flocculent and quite white, and has the following composition, expressed by $O[Hg'_2N(SO_3)Hg'_2]_2,6H_2O$:

	Calc.	Found.
Mercury,	77.22	77.27
Sulphur,	6.18	6.18

It is free from sodium. Although it contains water, it loses very little in weight at 100° or 120°, and part of that loss will be due to volatilisation of mercury, for the salt becomes very grey. More strongly heated, it becomes nearly black temporarily, soon growing white again. Then, or while still black, the altered salt gives some mercuric chloride, as well as mercurous chloride, when triturated with a solution of sodium chloride. At an incipient red heat the whitened altered salt fuses and effervesces, yielding nitrogen but no sulphur dioxide. The black-red liquid consists mainly of the mercury sulphates.

Mercurous imidosulphonate dissolves in dilute nitric acid much more readily than does mercuric imidosulphonate, and from the solu-

tion sodium chloride precipitates all the mercury. Rubbed with sodium-chloride solution, the salt becomes of a permanent, dull, and somewhat greenish orange colour, though quite free from the mercuric radical. The sodium-chloride solution becomes very alkaline to litmus, no doubt because of the formation of normal sodium imidosulphonate. Concentrated hydrochloric acid soon causes, even in the cold, the formation of some mercury and mercuric chloride, and, on heating, this change becomes complete.* Concentrated solution of potassium iodide at once in the cold dissolves it all but half its mercury, left as metal.

Normal sodium imidosulphonate converts it into mercury and the sparingly soluble mercuric sodium imidosulphonate. This fact it is which makes the normal sodium salt, otherwise desirable, not very well suited for preparing the mercurous salt. When it is used in place of the two-thirds normal sodium salt, each addition, however small and in however dilute solution, causes a blue-grey cloud of mercury to form, and consequently some mercuric salt. However, by incessant and violent stirring for ten minutes from the time of adding the normal sodium salt, not in excess, to the mercurous nitrate (which may here be used in a very dilute nitric-acid solution), the grey precipitate becomes almost completely white, and is then the mercurous imidosulphonate. Thus prepared, we have found it to contain 78.20 and 78.55 instead of 79.22 per cent. mercury, but the right quantity of sulphur, namely, 6.20 (twice), theory requiring 6.18 per cent.

The most probable constitution of oxymercurous imidosulphonate is that formulated as $O\begin{cases}Hg_2N(SO_3)_2Hg_2\\Hg_2N(SO_3)_2Hg_2\end{cases}, 6H_2O$, but other representations of it are, of course, possible.

* Owing to the production of amidosulphonic acid (see the following paper on this acid).

Mercurosic imidosulphonates.—Berglund found mercuric potassium imidosulphonate to have no noticeable immediate effect upon a solution of mercurous nitrate, but, on standing, the mixed solutions deposited some oxymercuric imidosulphonate. He must, therefore, have used a solution of mercurous nitrate containing an unnecessary quantity of nitric acid, for, with either reagent used in excess, precipitation is immediate, in presence of only a very little nitric acid.

The precipitate varies in composition with the proportions taken of the salts which form it, but still within well-marked limits. The variation is very great in the quantities of bivalent and univalent mercury, but very small indeed in the quantities of total mercury and of sulphur. The composition of the precipitates is such that they may be regarded as the oxymercurous imidosulphonate, just described, modified in having one-half to three-eighths of its mercurous radicals replaced by mercuric radicals, for it varies within the limits expressed by the formulæ—

$$O\begin{cases} Hg''N(SO_3)_2Hg'_2 \\ Hg''N(SO_3)_2Hg'_2 \end{cases}, 3H_2O$$

and

$$O\begin{cases} Hg''N(SO_3)_2Hg'_2 \\ Hg''N(SO_3)_2Hg'_2 \end{cases}, \quad O\begin{cases} Hg''N(SO_3)_2Hg'_2 \\ Hg'_2N(SO_3)_2Hg'_2 \end{cases}, 6H_2O.$$

They differ from the purely mercurous salt in having only half as much water of hydration. They cannot be represented as mixtures of the known oxymercurous salt with the known oxymercuric salt.

The compound, $O[Hg''N(SO_3)_2Hg'_2]_2,3H_2O$—(atomic ratios; $Hg''_4 : Hg'_8 : S_8$), is obtained by adding mercuric sodium imidosulphonate, a salt neutral to litmus, to half its weight of normal mercurous nitrate, which makes $3Hg''$ be present for every $2Hg'_2$, and leaves a neutral, or even alkaline, mother-liquor. The mercurous nitrate is used in the form described in the preparation of oxymercurous imidosulphonate.

After adding the mercuric sodium imidosulphonate to it, the mixture is well stirred, so as to insure the entrance into solution and chemical reaction of all basic mercurous nitrate, and until the mother liquor has just lost its acidity. The precipitate is white and settles quickly, and can be freely washed. When dry its colour is dull. It contains nearly all ($\frac{15}{16}$) of the mercury of the nitrate, but only $\frac{4}{7}$ of the mercuric radical, and even only $\frac{2}{7}$ of the imidosulphonic radical, its mother-liquor being very rich in imidosulphonate. This condition of the mother-liquor gives assurance that no mercurous nitrate can be in the precipitate and, in accordance with this, none can be found. Testing, however, for nitrate is interfered with by the presence of imidosulphonate. That the dry imidosulphonate does not effervesce in the least with cold strong sulphuric acid is best proof to ourselves of its absence (6, 77). Both precipitate and mother-liquor contain no sulphate.

	Calc.		Found	
Univalent mercury,	49.45	74.17	50.76	73.99
Bivalent mercury,	24.72		23.23	
Sulphur,	7.91		7.87	
Sodium,	—		0.04	

In the analysis, the two mercury radicals were estimated by dissolving the salt in dilute nitric acid, diluting the solution, precipitating mercurous chloride by dilute hydrochloric acid, and from the filtrate precipitating mercuric sulphide. After the salt has been hydrolysed in a sealed tube by hydrochloric acid, for sulphur estimation, the mercuric radical is found increased in quantity at the expense of the mercurous radical, and the oxygen in the air sealed up in the tube is shown, by the lessened pressure in the tube, to have been absorbed, and to have given rise to the increase of mercuric radical (see the

preceding paper by Hada on *How mercurous and mercuric salts change into each other*).

The compound, $O\begin{cases}Hg''N(SO_3)_2Hg'_2\\Hg''N(SO_3)_2Hg'_2\end{cases}$, $O\begin{cases}Hg''N(SO_3)_2Hg'_2\\Hg'_2N(SO_3)_2Hg'_2\end{cases}$, $6H_2O$

(atomic ratios; $Hg_3'' : Hg_{10}' : S_8$), is obtained by having the mercurous nitrate in excess, about 5 parts being taken for every 2 parts of mercuric sodium imidosulphonate, which provides $7Hg'_2$ for every $2Hg''$. The precipitate appears much the same as that obtained when the latter salt is taken in excess, and contains nearly $\frac{3}{4}$ of the mercuric and imidosulphonic radicals, but only a little more than $\frac{3}{5}$ of the mercury of the nitrate used. The mother-liquor is, accordingly, comparatively rich in mercurous salt; it is also acid. Mother-liquor and precipitate are free from sulphate, and the latter from nitrate. The dry precipitate is dull white.

	Calc.		Found	
Univalent mercury,	62.89	73.37	62.11	73.57
Bivalent mercury,	10.48		11.46	
Sulphur,	7.22		7.20	
Sodium,	—		0.01	

It will now be seen how remarkably the percentages of sulphur and of total mercury approach each other in the two precipitates, widely as the ratio of the two mercury radicals varies. We append the result of analyses of two other preparations; they support the conclusions drawn from the above extremes.

	A		B
Univalent mercury,	59.90	72.78*	73.46†
Bivalent mercury,	12.88		
Sulphur,	7.04		7.56

* This preparation was found to be damp when analysed.

† The numbers obtained for univalent and bivalent mercury in this case, namely, 51.98 and 21.48%, are in accordance with the others, but as they were determined in the salt after it had been hydrolysed, they are unreliable and therefore withheld from the table.

Amidosulphonic acid.

by

Edward Divers, M. D., F. R. S., Prof.

and

Tamemasa Haga, F.C.S., *Rigakuhakushi,* late Asst. Prof.

College of Science, Imperial University.

Amidosulphonic acid, erroneously supposed to be known nearly forty years ago, was not actually discovered and prepared by Berglund until 1876, and has only attracted the attention of chemists to any extent since 1887, when Raschig made known an easy process for its preparation in a new way.

The contents of this paper are a summary, not elsewhere found, of the work of others; new ways of forming the acid; a study of the interaction of oxyamidosulphonic acid and sodium amalgam, and of the same acid and sulphur dioxide; improvements of known methods of preparing amidosulphonic acid; a very productive and economical method of preparing it; undescribed properties of it; some new salts of it; remarkable points in the behaviour of its silver salt and mercury salt; and an investigation of the decomposition of the acid and its salts by heat.

Our colleagues, Professors Sakurai, Loew, and Takahashi have helped us in adding to what was known of the acid, by investigating, the first-named, its molecular conductivity, the other two, its physiological action. Both these investigations have a special interest, and form the subjects of separate communications following this.

Name of the acid.—Berglund accepted *sulphamic acid*, then in use, as an alternative name for the acid he had discovered, but employed that of *amidosulphonic acid*. This name, the use of which is now general, is analogically incorrect, and needs to be changed into either *amine-sulphonic acid* or *amidosulphuric acid*. Similarly, imidosulphonic acid and nitrilosulphonic acid should be altered to amine-disulphonic and amine-trisulphonic acids, or to imidosulphuric and nitrilosulphuric acids. But it seems of little moment to make the change, so long as ethylsulphonic acid remains in use in place of ethanesulphonic acid, and ethylsulphuric acid is misapplied to ethyl hydrogen sulphate. *Sulphamic acid* must remain in the back ground, until such time as sulphimic acid becomes acceptable for imidosulphuric acid, and some analogous name has suggested itself as suitable for nitrilosulphuric acid.

Formation of the acid.

1. Sulphur trioxide and ammonia, according to Berglund, sometimes yield a very little ammonium amidosulphonate along with the imidosulphonate, the chief product, when the ammonia is kept in large excess. He gives no details of his method of testing for it, and before he has stated that he has occasionally found it in very small quantity, he guardedly says that it probably can be formed in this way. The difficulty presents itself that even at 135° ammonium amidosulphonate begins to change into imidosulphonate, while the temperature caused by the union of sulphur trioxide and ammonia is much higher than that, and Berglund mentions that he did nothing to keep down the temperature. But, although the amidosulphonate does begin to change at so low a temperature as 135°, a little of it can remain unchanged at temperatures not very far below 300° (see the latter part of this paper). So that on the whole, when it is considered

that it was Berglund who first recognised that the product of the interaction of sulphur trioxide and ammonia is not amidosulphonate but imidosulphonate, it seems wise to accept his assertion as one well founded, that occasionally a very little real amidosulphonate is also formed.

2. Ammonium imidosulphonate readily hydrolyses into the amidosulphonate (Berglund, 1876). The imidosulphonate is obtainable from chlorosulphonic acid, from pyrosulphuryl chloride and sulphuryl chloride (after the action of water), as well as from sulphur trioxide, and ammonia.

3. Sulphamide, which is a product of the interaction of sulphuryl chloride and ammonia (Regnault; W. Traube), is decomposed by alkalis into amidosulphonate and ammonia (Traube, 1893).

4. By acting on acetonitrile with fuming sulphuric acid, a derivative of amidosulphonic acid is obtained, acetyl acetamidinesulphonic acid, which hydrolyses, with extreme readiness, into diacetamide and amidosulphonic acid (Eitner, 1892).

In the above four cases, amidosulphonic acid comes out as a sulphuric derivative; in those which follow, it comes from sulphur dioxide. In the first of them appear again imidosulphonates.

5. Nitrites, fully sulphonated by sulphur dioxide, become nitrilosulphonates, which very easily hydrolyse into imidosulphonates, and these, again, can be hydrolysed into amidosulphonates (Berglund, 1876). The hydrolysis of potassium imidosulphonate was studied by Fremy, and by Claus and Koch, long before Berglund, but without amidosulphonic acid being discovered by them. Its production was overlooked, no doubt, through the great solubility of its potassium salt, and through its ability to be destroyed by further hydrolysis.

6. Oxyamidosulphonic acid is produced by the hydrolysis of oximidosulphonic acid, which is formed by the sulphonation of a

nitrite; and, from this acid by reducing it with sodium amalgam, sodium amidosulphonate is obtained (Berglund, 1876). Berglund's work was admittedly incomplete; he did not isolate the acid and he did not state the condition for success. Oxyamidosulphonic acid is not attacked by sodium amalgam, except in acid solution; that it is then changed into amidosulphonic acid, we have proved by getting crystals of this acid. In place af sodium, zinc and sulphuric acid, as also the Gladstone-Tribe copper-zinc couple, may be used with perfect success. Another, but indirect, way of effecting the conversion is given lower down (10).

7. Potassium nitrososulphate, which is prepared from potassium sulphite and nitric oxide, and is not a sulphonate, also yields amidosulphonic acid among the products of its reduction by sodium amalgam. (See the paper, later on in this volume, entitled *The reduction of nitrososulphates*).

8. Simplest and most direct of all modes of formation of amidosulphonic acid is the sulphonation of hydroxylamine, which may be effected by allowing sulphur dioxide to act long enough upon a solution of one of its salts (Raschig, 1887).

9. Acetoxime also yields amidosulphonic acid by treatment with aqueous sulphur dioxide (M. Schmidt, 1891). Sodium metasulphite acts upon it to form a hydrolysable compound (v. Pechmann, 1887), which is dimethyl methyleneimidosulphonic acid (a monosulphonic acid, therefore, an amidosulphonic not imidosulphonic derivative); and it is this which by hydrolysis yields acetone again and amidosulphonic acid (Krafft, Bourgeois, and Dambmann, 1892).

10. The reduction of oxyamidosulphonic acid by sodium and by zinc has already been treated of (6), but this acid can also be converted by sulphur dioxide into imidosulphonic acid, from which amidosulphonic acid results by hydrolysis. That this would be

the case was recognised by Raschig, but he did not attempt to effect the change. We find that potassium oxyamidosulphonate mixed, in solution, with a molecule of potassium hydrogen carbonate and submitted to the action of sulphur dioxide, as in sulphonating potassium nitrite, is converted largely, and apparently completely, into the sparingly soluble, two-thirds normal potassium imidosulphonate, and under conditions like those of the sulphonation of hydroxylamine. For, the change is not immediate, but requires hours at the common temperature for completion, while at or near 0° it seems not to take place at all.

Methyl sulphate and ammonia do not form methyl amidosulphonatel as they were long supposed to do, but primary, secondary, and tertiary methylammonium sulphates and ammonium sulphate (Berglund, 1876). Ammonia acts, therefore, upon an alkyl sulphate, as Berglund pointed out, as it does upon an alkyl nitrate (Carey Lea, 1860).

Although the nature of the interaction of ammonia and methy, sulphate was discovered and worked out in detail by Berglund, his name is not even mentioned in connection with the subject in chemical literature, as represented by Beilstein's *Handbuch* and Morley and Muir's *Dictionary*. The whole credit of the discovery is given to Claesson and Lundvall, who, remarkably enough, dated their paper from Lund in 1880, only four years after Berglund's memoir on *amidosulphonic acid*, had appeared in that university town, and yet made no reference to it. In all points, so far as methyl sulphate and ammonia are concerned, Claesson and Lundvall had been anticipated by their countryman, except that, very usefully, they varied the experiment of dissolving the alkyl salt in ether and then passing ammonia gas into it, by first saturating ether with ammonia and then adding the sulphate gradually, and thus reduced to a minimum the production of the secondary and tertiary ammonium salts. The only

chemists who worked upon the action of ammonia upon methyl sulphate before Berglund were Dumas and Péligot in 1836, and they only observed that the two substances interact violently, when an aqueous solution of ammonia is added to the undiluted methyl sulphate, and, without quantitative analysis of the products, represented them to be methyl alcohol and methyl amidosulphonate ('sulphomethylane'). Strecker, in 1850, had, indeed, found that ethyl sulphate and ammonia combine together, but into a product which he called *ammonium sulphethamate;* and it used, therefore, to be supposed that the action of ammonia upon that sulphate was quite different from that upon methyl sulphate. Strecker, however, did observe that his complex salt gave ethylamine when heated, although from this weighty fact he deduced nothing.

Preparation of the acid.

Amidosulphonic acid may be advantageously prepared in two ways, one being based upon the sulphonation of hydroxylamine, and the other upon the hydrolysis of imidosulphonic acid. Both hydroxylamine and imidosulphonic acid are obtainable in several ways, but both of them best from the sulphonation of sodium nitrite and hydrolysis of the suitable sulphonate. It is, therefore, from sodium nitrite that amidosulphonic acid will, on economical grounds, be prepared, in either case. The production of the acid through imidosulphonic acid is much more profitable, as regards time, labour, and yield, than its production through hydroxylamine; but there must, for the present, be taken into consideration the facts that hydroxylamine hydrochloride is at hand in most laboratories, and that, beginning with it as the source, the preparation of the acid is easier than to begin with sodium nitrite. For, these facts will preserve the usefulness of the hydroxylamine

method until amidosulphonic acid itself becomes easily purchasable, as it should henceforth be.

Preparation from hydroxylamine sulphate.—Raschig's account of this process, using the hydrochloride, is brief and as follows:—'Saturate an aqueous solution of hydroxylamine hydrochloride with sulphur dioxide, allow it to stand some time, and then evaporate till a pellicle of crystals forms. A large quantity of the acid crystallises out by cooling, and the mother-liquor yields a little more, but mixed with ammonium sulphate.' Krafft and Bourgeois (1892) used the solution of hydroxylamine hydrochloride very concentrated, saturated it with sulphur dioxide to begin with and, for a day or two, supplied more as needed. In this way, they got the acid to crystallise without any evaporation, to the extent of fully three-sevenths of the calculated quantity. Although sulphur dioxide takes some hours to complete its action on hydroxylamine, it acts rapidly at first, and occasions a sensible rise of temperature. Cold checks its action; at 0° there appears to be none. Saturation of the hydroxylamine solution at this temperature with sulphur dioxide is sufficient, once for all, unless it is a very concentrated one, or is left exposed to the air. Some of the amidosulphonic acid gets hydrolysed, if the solution is evaporated on the water-bath, but not appreciably by evaporation in the cold.

Two points had to be investigated, one being as to whether the acid of the hydroxylamine salt had any influence upon the reaction, and the other, whether hydroxylamine and sulphur dioxide suffer complete conversion into amidosulphonic acid, or yield other products, such as ammonium sulphate, nitrogen, or nitrous oxide. The outcome of these investigations was that the action of sulphur dioxide is quantitatively the same upon the hydrochloride, the sulphate, and the base itself, and that ammonium hydrogen sulphate is a direct product of its action, and the only one besides amidosulphonic acid. Very

closely, about one-tenth of the hydroxylamine always becomes ammonia, the solution being cold (not much exceeding 25° by the heat of the reaction) and of moderate concentration. When the solution, a day after preparing it, is distilled with potassium hydroxide, it gives a tenth of the nitrogen as ammonia, whether sulphate or hydrochloride has been used, or whether or not, along with either of these salts, just enough sodium carbonate has been added to combine with its acid, leaving the hydroxylamine free, or whether more sodium carbonate has been added and converted into metasulphite. If, instead of at once distilling off the ammonia, the solution, deprived of its excess of sulphur dioxide, is heated for some hours at 150–60°, so as to hydrolyse all amidosulphonic acid, and only then distilled with potassium hydroxide, the ammonia obtained is closely equivalent to the hydroxylamine taken. Therefore, no nitrogen has been lost as gas. The stability of amidosulphonic acid is such that, under the stated circumstances, it is certain that only quite insignificant decomposition of the acid can occur, and, therefore, that nearly all the ammonium hydrogen sulphate comes directly from hydroxylamine, sulphur dioxide, and water.

Although the action of sulphur dioxide upon hydroxylamine is not affected by the acid present, there are several circumstances which make the sulphate more advantageous to use in preparing amidosulphonic acid than the hydrochloride, and therefore to be preferred to it. In the first place, the sulphate is easy to get in large crystals, on the small scale, and these are practically non-deliquescent, and it is a much cheaper salt than the other, when its preparation from sodium nitrite is effectively carried out ; in the second place, sulphuric acid (hydrochloric acid hardly) very greatly reduces the solubility of amidosulphonic acid in water.

To prepare amidosulphonic acid from hydroxylamine sulphate,

this salt may be dissolved in four or five times its weight of water, the solution nearly saturated ice-cold with sulphur dioxide, and set aside at the ordinary temperature for a day in a flask closed not quite air-tight. After it has thus stood, the sulphur dioxide remaining is to be expelled by a current of air, and the solution placed in a good desiccator, where the acid soon begins to crystallise out in thick plates. The crystals, well drained, are to be washed two or three times with a little ice water. The yield should approach four-fifths of the weight of the hydroxylamine sulphate. Since sodium nitrite can be converted inexpensively into its own weight of hydroxylamine sulphate, hardly a better source of the acid might seem possible to be had: nevertheless, it will never be resorted to in work on the large scale, for the acid itself can be obtained from sodium nitrite direct, more easily than hydroxylamine sulphate can be obtained from it. This process of getting it will now be described.

Preparation from sodium nitrite, through imidosulphonic acid.—Briefly, this process consists in fully sulphonating sodium nitrite by means of sulphur dioxide and sodium carbonate, hydrolysing the nitrilosulphonate to acid sulphate and amidosulphonic acid, neutralising with sodium carbonate, crystallising out sodium sulphate, and precipitating the amidosulphonic acid by addition of large excess of concentrated sulphuric acid. But to get the largest yield of acid most easily, some such particulars as the following must be observed. Sodium nitrite, 2 mol., and sodium carbonate, 3 mol., are put into enough water to make the whole weigh 18 times as much as the sodium nitrite; then sulphur dioxide is passed in until a solution acid to litmus is obtained. Most usually, the solution then very quickly changes of itself, but a drop of strong sulphuric acid may be added to start the change, which is that of the nitrilosulphonate into imidosulphonate and acid sulphate. Marked heating up occurs, and a large evolution of sulphur dioxide,

due to the interaction of the acid sulphate and sodium metasulphite, the latter salt having had to be produced in order to secure the sharp sulphonation of the nitrite (*This Journal*, 6, 66). Much of the loss of the sulphur dioxide, and of the inconvenience caused by its escape, can be easily avoided by distributing, at first, the nitrite solution in several flasks for separate sulphonation, and then allowing the sulphur dioxide regenerated by the hydrolysis of one portion to help in sulphonating another ; in doing so, the sulphur dioxide may be driven out by heating the hydrolysed solution, without detriment to it, if the heating is not too prolonged.

In any case, either a short heating is requisite, in order to hasten the second stage in the hydrolysis, (that of imidosulphonate into amidosulphonate and acid sulphate), or else a setting aside of the solution for a few hours (after expelling its sulphur dioxide by a current of air), in order to allow this hydrolysis to complete itself. The solution is next neutralised by adding one mol. sodium carbonate, that is, a third as much as the quantity taken at first, and the solution evaporated, by boiling or otherwise, until it again weighs only 18 times as much as the nitrite taken. Exposure of it then in an open vessel for a night, where it may fall to 0° or below, will make nearly all the sulphate present in it separate in large crystals, from which the mother-liquor can be well drained. With less evaporation or less cooling, further evaporation of the mother-liquor is needed to separate more sulphate, which seldom crystallises in so good form for draining. It is worth while to dissolve again the sodium sulphate in a third of its weight of water by heat and recrystallise it, to evaporate its mother-liquor to one-fifth and separate sulphate from it by cold, and then add it to the main quantity of mother-liquor.

The solution of sodium amidosulphonate, filtered from some turbidity usually present in it, is now mixed with concentrated sul-

phuric acid, $3-3\frac{1}{2}$ times the weight of nitrite taken, and set aside for a day in a cool place. Most of the amidosulphonic acid separates immediately,—what of the rest can be secured, crystallises out during the cooling and standing. It is well drained on porous tiles, and washed with a little ice-cold water.

The yield of acid by this process is affected by the tendency of the acid to form crystals with sodium hydrogen sulphate (see the account of the salts), and, therefore, sodium sulphate should be separated as much as possible, before adding the sulphuric acid. But a yield of 75 per cent. of the calculated quantity may be counted on, while much more can be obtained.

To get the acid pure and in good crystals, it must be recrystallised. This can be done, without considerable waste, by grinding it fine, adding it to $2\frac{3}{4}$ times its weight of boiling-hot water, and stirring diligently on a water bath until it is all dissolved. The solution set aside yields up about three-fifths of it, and the mother-liquor by cold evaporation will yield nearly all the rest in fine crystals, in spite of the hydrolysis which the hot water will have caused. Mother-liquors may also be worked up by precipitating the acid by means of strong sulphuric acid, or by alcohol.*

Properties of the acid.

Amidosulphonic acid is without odour or colour and has a sharp, purely acid taste (Berglund). From its aqueous solution it crystallises readily, and better than most of its salts (Berglund). Its crystals are orthorhombic plates; Fock (see Raschig's memoir) has examined it crystallographically, and shown it to be isomorphous with its potassium salt.

* For another, sometimes useful, way of preparing the acid, see p. 236.

We took its specific gravity, in ether, and found it to be 2.03 at 12°. Nothing has been published as to its melting point, except that M. Schmidt placed it as near 200°. It has, in fact, no real melting point, for, as will be shown later on in this paper, in the act of melting, it completely decomposes. Its apparent melting point, as near, probably as can be determined, is 205.° The observation of this point was made on the driest acid, in a capillary tube, beside a Jena thermometer with thread immersed, in a bath of sulphuric acid. It melts very slowly at this temperature. Even at its melting point, it begins to evolve vapours from its surface, but these are of its decomposition products, and very slight in dry air. In fact, this volatilisation and the melting point are greatly affected by the access of moist air, and by any dampness in the acid used.

Berglund described it as being quite easily soluble in water, and it is so, though slowly. But it is less soluble than any of its salts, except that of silver (not counting its basic mercury salt). It requires 5 parts of water at 0°, and $2\frac{1}{2}$ parts at 70°, to dissolve it. The fact, that hot water is not without chemical action upon it, renders a close determination of its solubility in hot water impossible. There is no known solvent for it but water.

Sulphuric acid greatly diminishes the solubility of the acid in water, and readily precipitates it from its solution, and from solutions of its salts. Its solubility in water is also greatly reduced by the presence of sodium hydrogen sulphate. These facts largely facilitate the preparation of the acid, as already described. Not more than 3 parts of acid per hundred of water remain in solution after concentrated sulphuric acid, $\frac{1}{5}$—$\frac{1}{4}$ of the volume of solution, is added, and the solution left to itself for a day. A 5 per cent. solution of the acid very soon deposits some of it, when mixed with sulphuric acid; a $2\frac{1}{2}$ per cent. solution deposits none, even on standing, but, when previously

nearly saturated with sodium hydrogen sulphate, it yields some of its acid on standing, after admixture with sulphuric acid. Nitric acid also precipitates amidosulphonic acid from its solution, but to a much less extent than sulphuric acid. A fuming solution of hydrochloric acid does not precipitate it. Glacial acetic acid acts well as a precipitant, but more of it must be used than of sulphuric acid. It is stable in the air (even when crude) and non-deliquescent in the cold, but it generally holds about one per cent. of water, either hygroscopically or to a slight extent as ammonium acid sulphate. It is also stable in cold solution (Berglund), or very nearly so. Dilute hydrochloric acid and barium chloride along with it do not seem to lessen its stability in the cold. A solution of the acid may be boiled for a moment or be kept at 100° for a very few minutes, and still fail to show sulphuric acid with barium chloride. At 45° there is just enough hydrolysis in 2 hours to give a turbidity with barium chloride in 20 seconds. The presence of hydrochloric acid in a boiling solution quickens the destruction of the acid very much, but does not quite complete it in the course of a few hours. Heating to 150° makes the hydrolysis complete in presence of hydrochloric acid, in three or four hours (Raschig). Berglund stated that the acid in aqueous solution can be boiled for an hour without decomposition occurring, though continued boiling decomposes it ; and that, though hydrochloric acid hastens matters, the solution may be boiled with this acid and barium chloride for an hour, before barium sulphate begins to separate. Also Raschig stated that in its boiling solution, the acid is practically undecomposed, and only very slowly decomposed in presence of acids.

According to our experience, just recorded, Berglund and Raschig have magnified the degree of stability of the acid in boiling solutions. Krafft and Bourgeois, on the other hand, magnified still more its

instability when, in purifying the acid, they only ventured to dissolve it in slightly warm water.

Crystals of the acid will lie for months in concentrated sulphuric acid unchanged; heated with it till dissolved, the acid undergoes essentially the same change as when heated by itself. Berglund found the acid not to be decomposed by boiling with potassium hydroxide; while, according to Raschig, alkalis seem to make the acid more unstable. We find the decomposition caused by continuous boiling to be very slight, and no greater than that in a solution of the neutra potassium salt kept at the same temperature. Alkalis appear, therefore to be inactive. A solution of the potassium salt along with potassium hydroxide can be evaporated on the water bath, without the salt suffering noticeable change. Were it otherwise, how could sulphamide, boiled with alkali, produce amidosulphonate, half the nitrogen only escaping as ammonia (Traube)?

Heated in ordinary damp air to 100°, amidosulphonic acid very slowly fixes water, through hydrolysing, and becomes sticky on the surface of its crystals. Krafft and Bourgeois found this change to proceed freely at 130–140°. Berglund, on the contrary, found that the acid does not change in this way until at 190° or above; but the facts observed by Berglund are such as occur without the intervention of moisture, as will be made clear when the effects of heating the acid are described.

Amidosulphonic acid retards the precipitation of small quantities of sulphuric acid by barium chloride, a fact that must be taken into account when testing for the beginning of decomposition of the acid itself. A cold saturated solution of amidosulphonic acid, containing one part sulphuric acid in 10,000 water, gives no precipitate for some minutes after barium chloride solution is shaken with it, and then only slowly and sparingly, though in 20 hours precipitation seems to be

nearly complete. With only half as much sulphuric acid present, barium chloride takes half an hour to cause any precipitation, and this remains very slight for a long time. In strong, neutral or alkaline solutions, alkali amidosulphonates also retard, for a day or two, the complete precipitation of a sulphite by barium chloride. Amidosulphonic acid with sodium changes into its sodium salt and hydrogen. It dissolves zinc and iron (Berglund). It does not decompose an alkali chloride or nitrate, when mixed with the salt in the damp state or in solution. Heated dry with the salt, it causes decomposition, but then the acid is itself decomposed.

Amidosulphonic acid is decomposed with effervescence, even at the ordinary temperature, by a mixture of concentrated sulphuric acid and a nitrate or nitric acid, the gas being nitrous oxide. In this respect, its behaviour is like that of imidosulphonic acid, which, in 1892, we fully described, on page 77 of our paper on *Imidosulphonates* (*This Journal*, 6). Soon after issuing that paper, we recognised the similarity of this reaction with that discovered by Franchimont (1887), —that by which nitramide has recently been obtained by Lachmann and Thiele (1896). But we were, at that time, unable to study the reaction further. Lachmann and Thiele have been the first to publish the fact that amidosulphonic acid gives nitrous oxide when treated with nitric and sulphuric acids. They also state that nitramide itself cannot be got by the reaction, but they give no particulars. We, too, have failed to get any nitramide, not, apparently, because it is decomposed after being formed, but because there is no action between the nitric and amidosulphonic acids in a freezing mixture. As already mentioned, amidosulphonic acid is quite insoluble in strong sulphuric acid and but little soluble in the dilute acid. Owing to this property, we have been able to recover from a mixture of the acids, which had been stirred up for nearly an hour, immersed in ice and salt, not only

much of the nitric acid (by ether extraction), but also much of the amidosulphonic acid, by getting it deposited when the mixed acids, holding it suspended, were poured upon ice to dilute them. In our experiments, we used the amidosulphonic acid in form of its ammonium salt, with the object of having the acid present in the finest state of division.

As has just been indicated, amidosulphonic acid is oxidised in the cold by nitric acid in presence of concentrated sulphuric acid. It is also oxidised by hot or even cold nitric acid, by potassium chlorate and hydrochloric acid (Berglund), and by chlorine and bromine. It is not acted upon by chromic acid or permanganic acid solution or by ferric chloride, ferric amidosulphonate being as stable in hot solution as the other salts of the acid. But the acid is slowly oxidised, at a boiling heat, by silver oxide and alkali, and then silvers the glass. This oxidation gives the solution the power, when acidified, of reducing small quantities of permanganic acid. This property, together with the fact of sulphites in alkaline solution not being oxidisable by silver oxide, makes it pretty certain that the reduction of silver goes on thus (but see the account of the silver salt, p. 239) :—

$$H_2NSO_3K + Ag_2O = AgSO_3K + Ag + N + OH_2.$$

Platinum black very slowly acts upon a solution of amidosulphonic acid, exposed to the air, and produces sulphuric acid, but, apparently, only by hydrolysis.

Amidosulphonic acid prevents the precipitation of silver and mercuric salts by alkalis (see the accounts of the silver and oxymercuric salts, pp. 239 *et seq.*). Here the acid is seen acting as an amine.

It combines with boiling alcohol, in the course of hours, and becomes ammonium ethyl sulphate (Krafft and Bourgeois). Boiled with aniline, it is slowly and similarly converted into ammonium

phenylamidosulphonate (Paal and Kretschmer, 1894). Both reactions are analogous to the hydration of the acid, NH and O functioning alike.

Its behaviour when heated dry will be found described after the account given of its salts.

Preparation and properties of the salts.

A number of the salts of amidosulphonic acid were examined by Berglund, and a comparatively full account of his work upon them, condensed by Clève from Berglund's Swedish memoir, was published in the *Bulletin*, **29**, 422. The salts examined were those of potassium, sodium, lithium, ammonium, thallium, silver, barium, strontium, calcium, lead, nickel, cobalt, manganese, zinc, cadmium, and cupricum, and the existence of a basic mercuric salt was pointed out. Raschig prepared again and analysed the potassium salt, and included, in his account of it, its crystallographic elements, as determined by Fock. Krafft and Bourgeois again analysed and described the barium salt; Eitner again analysed the barium and the silver salts. Paal and Kretschmer again analysed and described the silver salt (acknowledging the previous work of Eitner), the copper salt, and the lead salt. Of these investigators, Raschig alone mentions Berglund, carefully indicating the great value of his work. The others are silent as to the work of the chemist who not only first prepared the acid and its salts, but analysed and described them, at least as fully as they have done. Yet an epitome of Berglund's paper, drawn up by himself, appeared in the *Berichte* of the German Society (and not among the *Referate*), besides appearing, in another form, in the *Bulletin* of the French Society, as we have just said.

Now that the isolation of the acid has become easier than that of any of its salts, the work of Berglund and of Raschig, upon the prepara-

tion of the salts, has lost its value. Berglund, by laborious processes, prepared the barium salt by hydrolysing either the barium or the mercury barium imidosulphonate, and from this obtained the acid and the other salts. He gave himself unnecessary trouble through his belief, founded on observation, that imidosulphonates have a great tendency to pass at once into ammonium sulphate, instead of stopping at the stage of amidosulphonates, although these, once formed, are stable enough. Instead of describing Berglund's, now obsolete, process, we will give a very simple modification of it that may sometimes prove useful.

Normal barium imidosulphonate, freed from alkali by re-precipitation, is kept on the water bath, with very slightly more dilute sulphuric acid than is equivalent to one-third of its barium, just so long as a little of the filtered solution is found to yield barium sulphate on boiling ; then, after filtering off and washing the barium sulphate, the solution of amidosulphonic acid is evaporated in the cold over sulphuric acid.

Nothing need he said of the preparation of the salts from the acid. A line or two may be given to the direct preparation of the sodium and potassium salts from the nitrite. If, in the preparation of the acid from sodium nitrite, already described, the mother-liquor from the sodium sulphate crystals is further evaporated, sodium amidosulphonate crystallises out, and can be thus obtained. But from the smallness of the crystals and their great solubility, they are badly obtained from an impure solution, and it is far better to prepare the salt from purified acid and sodium carbonate. Raschig obtained the potassium salt direct, in the above way. Other amidosulphonates cannot be prepared by double decomposition of the alkali salts (see the account of the silver salt, p. 239).

All amidosulphonates (except the oxymercuric) are soluble in water, the least soluble of them being the silver salt (Berglund). Most

of them are exceedingly soluble, and form supersaturated solutions (Berglund). They are stable, even in solution, so far as we have observed, except the ammonium salt, which is liable to hydrolyse, if not quite dry. Their solutions may be kept for hours at 100°, or even be boiled, without showing decomposition. The behaviour of some of them, when heated in absence of water, will be described after that of the acid itself.

A double salt of sodium sulphate and amidosulphonic acid has been obtained by us at times in the course of preparing amidosulphonic acid and separating it from its sodium salt by sulphuric acid ; but experiments, made to determine the conditions for its production at will, have been unsuccessful. When obtained by us, it had crystallised from a strongly acid solution, and formed short, thick prisms, somewhat deliquescent. Its analysis showed it to have the composition of 6 mol. amidosulphonic acid with 5 mol. disodium sulphate, and 15 mol. water.

	Calc.	Found.
Sodium,	14.72	14.79
Sulphate sulphur,	10.24	10.18
Sulphonate sulphur,	12.29	12.08
Water,	17.28	15.70

This complex may have been only a crystal compound, but it could not have been a mere mixture, because of its form, its apparent homogeneity, and its content of water. It may be written as— $H_2NSO_3H+5(NaO.SO_2.NH_2.HO.SO_2.ONa, 3OH_2)$, which, if the one mol. of amidosulphonic acid be neglected, is a salt analogous to the well-defined and stable ammonium sodium sulphate, formed under similar circumstances, the sodium amidosulphonate representing am-

monia. In our accounts of imidosulphonates and oximidosulphonates, already published, we have had occasion to point out the apparent functioning of these salts as amines towards nitric acid.

Hydroxylamine amidosulphonate has only been obtained as an uncrystallisable viscous hygroscopic liquid. It was prepared by decomposing hydroxylamine sulphate by its equivalent of barium amidosulphonate.

Ferrous amidosulphonate.—This salt was prepared from the acid and iron-wire, with exclusion of air. Since the solution of this very soluble salt has to be evaporated *in vacuo*, it is well to use much less water than would dissolve all the acid, for this then goes into solution in proportion as it is consumed by the iron. The solution and crystals have the usual blue-green colour. The solution shows supersaturation, like many other amidosulphonates, and the salt is consequently obtained in the form of a cake of radiating prisms, just like the zinc salt. It is deliquescent, and, unlike the sulphate, is not precipitated by alcohol. Pressed in filter paper, but still slighty damp, some of the salt showed, by permanganate, the presence of 16.48 per cent. of iron. A salt with $4OH_2$ would have 17.5 per cent. of iron and one with $5OH_2$, 16.57 per cent. The latter must, we think, be taken as the right expression. Analogy is not available for deciding the point, for, according to Berglund, though the zinc salt has $4OH_2$, the nickel, cobalt, and manganese salts have $3OH_2$, the cadmium salt, $5OH_2$, and the copper salt, $2OH_2$. The magnesium salt has not been prepared.

Ferric amidosulphonate.—This salt was prepared by dissolving ferric hydroxide and the acid in water. Its solution is of a bright brown colour and dries up into an opaque, amorphous, brittle mass, of the colour of ferric hydroxide. It is very soluble in water but is not at all deliquescent. It has the full astringent taste of the ferric salts of inorganic acids, not that of the citrate or tartrate.

The silver salt.—Before passing to the results of our own examination of the important silver salt, we give Berglund's excellent account of it. 'It crystallises best of all the salts; it is also the least soluble, requiring about 15 parts of water at the ordinary temperature (19°). It forms bundles of striated prisms, looking much like those of the sodium salt, and almost as hard and brittle as glass. It blackens only extremely slowly; its solution is quite neutral. It is best prepared from barium amidosulphonate and a solution in boiling water of its equivalent of silver sulphate.' (Then follows its analysis, showing it to be anhydrous). With the acid itself at disposal, the above mode of preparing the salt will never be adopted. The hardness and brittleness of the crystals are no more noticeable than in crystals of silver nitrate or of amidosulphonic acid; Berglund was impressed by these properties, probably, because most amidosulphonates form delicate fibrous crystals.

Silver amidosulphonate cannot be prepared from the potassium salt and silver nitrate. The most concentrated solutions of these salts, mixed in molecular proportions, yield no crystals, even in contact with one of silver amidosulphonate itself. Thus, we may prepare a solution equivalent to that of the salt in twice its weight of water, although the salt is not soluble in less than fifteen parts. Such a solution, with a crystal of the silver salt in it, dried up in the desiccator, gave three kinds of crystals; some were silver amidosulphonate in combination, apparently, with nitrate; others were potassium nitrate; and the rest in opaque prisms, were silver potassium amidosulphonate nitrate. The unreadiness here displayed by the potassium, to give place to silver, is more strikingly manifested in the behaviour of the silver salt towards alkalis.

Potassium hydroxide added to a solution of the silver salt, not too dilute, gives a bright yellow-ochre precipitate, in tough, granular

particles. The potassium hydroxide being in moderate excess, the mother-liquor is bright yellow, like a solution of gold chloride. Both precipitate and solution are changed by much water; they become brown, and the precipitate dissolves. Either solution gives a brown precipitate when heated, or when mixed with excess of potassium hydroxide, or silver nitrate, or potassium amidosulphonate, and this precipitate cannot be redissolved. The yellow solution is also unstable, gelatinising on long standing, and leaving a colourless solution. Yellow and brown precipitates and solutions appear all to be colloidal in character. The brown substance in solution and the brown precipitate are apparently silver oxide essentially. The yellow compound is not blackened by light, is soluble without colour in potassium amidosulphonate, and is slowly converted to a whitish, pulverulent precipitate by digestion with silver-nitrate solution, and into a white flocculent precipitate by excess of potassium hydroxide. Its solution in a minimum of potassium amidosulphonate silvers glass at a boiling heat. So does a solution of potassium amidosulphonate, silver nitrate, and potassium hydroxide. As already stated, sulphite appears to be produced in this reduction of silver.

A solution of silver amidosulphonate does not sensibly dissolve silver oxide. Silver nitrate behaves in solution with its equivalent of potassium amidosulphonate like silver amidosulphonate towards potassium hydroxide. If the silver nitrate is present in excess, and the solution not too dilute, precipitation of the amidosulphonic compound precedes that of silver oxide. If the proportion of potassium amidosulphonate is as two mol. to one of the silver nitrate, potassium hydroxide causes no precipitate in solutions of moderate concentration; that is to say, amidosulphonic acid prevents the precipitation of silver oxide by alkalis. A solution of 2 mol. potassium amidosulphonate, 2 mol. potassium hydroxide, and 1 mol. silver nitrate dries up in the desic-

cator into a white, homogeneous mass of minute, silky fibres, soluble again in water unchanged. Alcohol extracts from it no significant quantity of potassium hydroxide.

Further experiments are necessary to justify us in speaking positively and these, for the time, are impossible. But there can be little doubt, from what has been already ascertained and from analogous facts, that one of the amido-hydrogens is replaceable by silver, and even by potassium ; that the ochre-yellow colloidal substance, soluble in water (when it is neither too much nor too little), is $AgHNSO_3K$; and that the white, fibrous, very soluble salt is a compound of silver potassium amidosulphonate with dipotassium amidosulphonate ($KHNSO_3K$) and potassium nitrate. The power of preventing the precipitation of silver salts by alkalis exhibits amidosulphonic acid playing the part of an amine. It has no solvent effect in the case of cupric salts ; in that of cuprous salts, its action has not yet been tried. The reduction of silver by amidosulphonic acid has been already briefly discussed along with the other properties of the acid.

Mercurous amidosulphonate cannot exist. The acid gives with a solution of mercurous nitrate a precipitate of metallic mercury and the salt next described.

Oxymercuric amidosulphonate.—Berglund recorded that silver amidosulphonate gives with mercuric chloride a mixed precipitate of silver chloride and basic mercuric amidosulphonate and sets free some amidosulphonic acid. The normal salt cannot be obtained. When mercuric oxide and amidosulphonic acid are ground together and moistened, they slowly interact, so that, with occasional stirring, the action is complete in two or three days. But they produce only the oxymercuric salt, $(H_2NSO_3HgO)_2Hg$, $2OH_2$, any excess of acid dissolving out in water, without taking any mercury with it, and any excess of mercuric oxide, evident by its red colour, being removable by

digestion with much diluted nitric acid. Mercuric chloride and potassium amidosulphonate mix together in solution without change, but, with the former not in excess, potassium hydroxide, in quantity not exceeding the equivalent of the chloride, gives rise to the above salt, as a white precipitate. The acid can precipitate almost all the mercury from a solution of mercuric nitrate, leaving only nitric acid in solution; and is itself completely precipitated by a slight excess of mercuric nitrate.

To prepare the salt, it is best to mix a dilute solution of the acid with a concentrated solution of mercuric nitrate in the minimum of nitric acid, when the salt forms as a snow-white, voluminous, and very finely divided precipitate, troublesome to wash, either by decantation or on the filter, and taking long to dry on the tile, all in consequence of its fineness of division. It is very stable and may be washed with hot water. Air-dried, at the common temperature, it contains two mol. water, which it easily loses when heated (at 115°). The results of its analysis are as follows:—

	Calc.	Found.
Mercury,	69.77	70.80
Sulphur,	7.44	7.49
Water,	4.19	4.65

The mercury found is too high through imperfect determination; for, when calculation is made, the total a little exceeds 100. The error does not affect the formula adopted.

The salt requires comparatively strong nitric acid to dissolve it in the cold. Hydrochloric acid dissolves it, of course; but, what is very remarkable, potassium hydroxide does so, too. By using an insufficient quantity of alkali, it is possible to decompose the salt partly, and thus to get a little yellow mercuric oxide from it, which remains

insoluble in excess of alkali. But when the alkali, in excess, is rapidly mixed with it, the salt all dissolves permanently. Mercuric chloride, in presence of enough amidosulphonic acid, is not, therefore, precipitated by potassium hydroxide in excess ; addition of more mercuric chloride, or of a little acid, causes the white oxymercuric salt to precipitate, but not mercuric oxide.

The precipitation of the oxymercuric salt from an acid solution of mercuric nitrate indicates its nature as a basic salt, while in degree of basicity it agrees with the oxymercuric salts of sulphuric, sulphurous, and imidosulphonic acids, that is, it possesses the bivalent group, –OHgOHgO–. But the stability of the salt when heated (see later on), its insolubility in dilute nitric acid, and its solubility in an alkali suggest the possibility of its having another constitution, or of its being subject to tautómery. At least, in its alkaline solution, it must almost certainly exist as a potassium salt with the following formula, $Hg''_3N_2(SO_3K)_2(OH)_2$, which exhibits it as a sulphonated mercurammonium hydroxide. Like other mercurammonium salts, it does not yield up its amine (amidosulphonic acid), when treated with alkalis. It also behaves like a mercurammonium compound, in being completely resolved, in accordance with Pesci's reaction, into amidosulphonic acid (its amine) and mercuric bromide by a saturated solution of ammonium bromide, ammonia being liberated, thus :—

$$Hg_3N_2(SO_3H)_2(OH)_2 + 12NH_4Br = 3[HgBr_2(NH_4Br)_2] + 2NH_2SO_3NH_4 + 4NH_3 + 2OH_2.$$

The action of a dilute solution of ammonium chloride is to convert it only into 'white precipitate' and a solution of mercury ammonium chloride and ammonium amidosulphonate, without any ammonia being liberated.

The oxymercuric salt bears heat well ; its decomposition at a high temperature will be described in the next section.

Effects of heating amidosulphonic acid and its salts.

The acid.—The only statement yet made, concerning the effect of heating amidosulphonic acid in the absence of water, is Berglund's that, when the acid is rapidly and sufficiently raised in temperature, it is decomposed, and that sulphur dioxide, nitrogen, water, and sulphuric acid are produced. That statement is correct, though it is remarkable that ammonia is not mentioned in it, since this, in combination, always appears among the products. But much below the temperature at which the acid passes into these products, it suffers a complete che ical change. This occurs largely when the acid appears to melt, that is at 205°. In a closely limited space, to which air has not free access, it sustains no loss in half an hour, when heated to 220°, and only about 1 per cent. when heated to 260°. Just above 260°, small bubbles very slowly form in the liquid, but become reabsorbed if the temperature is lowered ; they consist, almost certainly, of ammonia. There is much expansion in the act of melting, for the unmelted particles sink freely in the melted part. The liquid forms a vitreous mass, on cooling, which contracts so much as to partly detach itself from the glass, even cracking this when very thin. The vitreous product is brittle, exceedingly deliquescent, and very soluble in water. Kept dry, it shows no tendency, in several days, to crystallise, and remains quite transparent.

Although the vitreous mass, obtained by fusing the acid, must have the same ultimate composition as the acid itself, it yet contains very little of the acid left. The predominant substance found, when the mass is dissolved in water, is ammonium hydrogen sulphate. More than half the quantity of the acid, that has been fused, comes out then as the acid sulphate, that is, has combined with the elements of water. Such a result, as the effect of heat alone, is plainly impossible,

and must, therefore, be in part, at least, due to the action of water in dissolving the mass. This can easily be shown to be the fact, but in doing so, it becomes established that nearly half the acid is actually converted into sulphate, by heat alone. For, when the mass is dissolved in a solution of potassium hydroxide, sulphuric acid and ammonia are still the principal products. But the proportion of the former is now not so great as before. In the alkaline solution, and sometimes separating out from it in crystals, there is present another product in large quantity, which is imidosulphonate. Since the quantity of ammonia is the same, whether the mass is dissolved in presence of potassium hydroxide or in its absence, and since it is too large to make only its acid sulphate with the sulphuric acid present in the alkaline solution, it follows that some of the ammonia must exist in the vitreous mass as ammonium imidosulphonate. The composition of the alkaline solution at once explains how more sulphuric acid is got by dissolving the product in the absence of alkali than in its presence ; for acid imidosulphonate very rapidly hydrolyses into sulphate and amidosulphonic acid. Accordingly, it is found that what, in the acid solution, is not ammonium hydrogen sulphate is amidosulphonic acid itself ; while, in the alkaline solution, so much of the sulphur may be present as sulphate and imidosulphonate as to leave only a little to be accounted for as amidosulphonic acid, also present. It is now evident, since water from without does not enter, that, in the production of ammonium sulphate by heat alone, one part of the acid must yield the elements of water to the other part, and remain itself as imidosulphonate, for nothing escapes during the heating. This is only possible by both sulphate and imidosulphonate coming into existence as their pyro-salts, neither of them a yet known salt or isolable from the vitreous mass. But there is nothing to be said against this assumption ; and the analytical dat upoint, without

alternative, to the presence in the vitreous mass of these two pyro-salts in molecular proportions, along with some unchanged amido-sulphonic acid. The following equation expresses the formation of the pyro-salts :—

$$4H_2NSO_3H = (NH_4SO_3)_2O + NH_4N(SO_2)_2O.$$

The formation of acid imidosulphonate,—$4H_2NSO_3H = 2NH_4N(SO_3H)_2$, and that of pyrosulphate,—$4H_2NSO_3H = (NH_4SO_3)_2O + (H_2NSO_2)_2O$, are not necessarily simultaneous ; but, within the limits of analytical determination, appear to be so. In the case of some amidosulphonates, however, the conversion to imidosulphonate partly precedes that into sulphate.

We now give such particulars of the analysis of the mass, and of the calculation of the results, as seem to be necessary. Heating the acid in a vessel only loosely covered is out of the question, because of its avidity for moisture when fused or near its melting point. Heating over the direct flame is also almost unmanageable. The operation was found to become quite simple by using thin-walled tubes closed at one end, about 5 mm. wide and 70 mm. long, closely plugged with glass rod, but not air-tight. About a gram of acid served for an experiment. Heat was imparted by a sulphuric acid bath, slowly raised in temperature. The tube and vitreous mass were reweighed when cold again, as a precaution. The mass dissolved in water and distilled with alkali gave the quantity of ammonia in it. Dissolved in water and left to stand for some hours, then heated almost to boiling, and precipitated by barium chloride, the mass contained in another tube gave the sulphuric acid compounded of that formed by heat alone and that subsequently formed by dissolving the mass in water. Hydrolysis at 150° of the filtrate and addition of more barium chloride gave the rest of the sulphur, and thus served as a measure of the quantity of

real amidosulphonic acid used, apart from any water that might have been absorbed by it before it was weighed. An important factor in determining the constitution of the product is its original acidity ; its acidity after hydrolysis of the imidosulphonate to amidosulphonate is unimportant, being the same as that of the amidosulphonic acid taken. The acidity before hydrolysis was ascertained by dissolving the mass in a suitable manner, as follows, in volumetric potassium hydroxide and titrating. As nearly as convenient, a cgm. mol. of the acid was taken and fused, so that 10 cc. normal potassium hydroxide might be the quantity of alkali to be measured. This quantity of alkali, placed in a 20 cc. stoppered bottle, was cooled in ice. The tube was broken on a plate of glass by tapping it with a mallet, so as to expose much of the fused lump, and then this, along with all fragments of the tube which had been in contact with it or near it, was most expeditiously dropped into the potassium hydroxide. The stopper being firmly inserted, the bottle with its ice-packing, was, without a moment's delay, shaken and kept violently agitated until dissolution of the mass was complete. With its stopper loosened, the bottle was placed in a beaker containing water and 5 cc. normal hydrochloric acid, then opened, and its acidified contents titrated, with methyl orange as indicator.

In calculating the results, the amount of either sulphuric acid or ammonia is enough to know, that of the other serving only as a check of the accuracy of its determination, for the two amounts could not but be equivalent. If all the acid were changed by heat, but only into the one-third normal ammonium imidosulphonate, $NH_4N(SO_3H)_2$, the hydrolysis of this, exactly into imidosulphonate and sulphate, would give half the sulphur and the nitrogen of the amidosulphonic acid as sulphuric acid and ammonia (so it would, if all the acid were changed half into amidosulphonic anhydride, half into ammonium pyrosulphate). If all the acid were changed into ammonium pyroimidosul-

phonate and pyrosulphate, the hydrolysis of these would give three-fourths of the sulphur and nitrogen as sulphuric acid and ammonia. Partly one and partly the other change would give proportions intermediate to one-half and three-quarters of the sulphur and nitrogen. But, if any of the acid were to remain unchanged by the heat, uncertainty, as to the relative extent of the two possible changes, would be caused. The degree of acidity of the mass removes this uncertainty, for, whereas this is less than that of the amidosulphonic acid to the extent that these changes have occurred and developed ammonia (neutral imidosulphonates being the two-thirds normal salts), the unchanged acid retains, of course, its full acidity. Any excess of acidity of the mass over that equivalent to its ammonia is, therefore, a measure of the quantity of the unchanged acid. Since, finally, the amounts of ammonia and sulphuric acid prove to be the equivalents of three-fourths of the nitrogen and sulphur of the changed part of the acid, it becomes known that the change is wholly into the pyro-salts.

There is another method of testing the vitreous mass, which is not without importance from a qualitative point of view, and which is one that may be used for a half direct estimation of the imidosulphonate and sulphate. If to the cold, somewhat alkaline and unhydrolysed solution, barium chloride is added so long as it precipitates anything, the precipitate contains not only the original sulphate but almost all the imidosulphonate. Much of the barium imidosulphonate could be dissolved out by ammonium chloride, but to effect an approximate determination of the composition of the precipitate, it is better to wash it with warm water till it begins to pass the filter, then wash it off the filter, boil it for a minute with very dilute hydrochloric acid, and filter off again through the same filter, keeping the filtrates separate. The precipitate is washed with hot water till it again begins to pass the filter, then dried, ignited, and weighed as sulphate. The amidosul-

phonic acid which has been extracted from the original precipitate (along with some barium) is then to be estimated by concentrating the second filtrate and washings and heating at 150° in sealed tube, to convert the amidosulphonic acid into sulphuric acid, which is, lastly, weighed as barium salt. This represents half the sulphur present in the original precipitate as imidosulphonate ; when, therefore, its weight is deducted from that of the sulphate got from that precipitate by the treatment with hydrochloric acid, the difference is the sulphate present in the vitreous mass. We made use of this method, with sufficient success, in the earlier work done upon it.

The extent to which the acid is decomposed by heating it to about 220° or to 265°, for twenty to thirty minutes, hardly varies from 93 per cent. (corrected, probably 90 per cent.), as the following comparison shows.

	Calc.	220°	265°	265°
Sulphate sulphur (incl. that by hyd.)	23.01	23.04	23.02	—
Sulphate sulphur (by heat alone)	15.34	—	—	15.53
Ammonia nitrogen,	10.06	10.00	10.15	—
Residual acidity,	76.75	76.73	—	77.00

But as the acid used had always with it at least one per cent. water, partly as moisture, partly combined as ammonium hydrogen sulphate, it is probable that the decomposition of the thoroughly dry acid would extend to less than 90 per cent. of it. This is, however, hardly, a point of consequence.

On heating the acid much above 260°, the products first formed enter into decomposition. A portion of six or eight grams melted and further heated, over a small flame, in an open platinum crucible, forms large tenacious bubbles, until somewhat more than a tenth has boiled

off. The temperature rising, the liquid becomes quite thin, while fine effervescence and free ebullition set in; probably, colloids have now changed to crystalloids by hydration. On removing the flame, the boiling quickly stops, but the effervescence continues for some time. The vapours evolved at first are dense white and apparently contain much sulphur trioxide, besides dioxide diluted with much nitrogen; but, as the temperature rises and decomposition gets more rapid, the vapours become almost transparent. They can then be copiously condensed on a glass plate held over, but not touching, the mouth of the crucible, and form on it a dense white, crypto-crystalline, dry, coherent, non-deliquescent film, neutral or even slightly alkaline to litmus. The substance thus deposited is ammonium pyrosulphite. Towards the end of the decomposition, with further rise of temperature, ammonium hydrogen sulphate condenses from the vapours.

If the liquid is allowed to cool when something like a fourth of it only has been driven off, large prisms shoot right across the solidifying mass, suggesting the crystallisation of a less fusible salt out of its solution in a more fusible one. These prisms are probably ammonium hydrogen sulphate. When the heating is not arrested till half or more of the liquid has been volatilised, the mass on cooling consists of brilliant prismatic plates.

The decomposition induced by the higher heating is an interesting sequel to the primary decomposition of the acid by heat. That consisted in a part of the elements of water and ammonia becoming available in hydrating and forming salts out of the acid. The succeeding change proceeds with the same consequences, but the water and ammonia are now obtained only by sulphur oxides, nitrogen, and a little ammonia being lost by the mass. The pyro-salts become ordinary salts in the following way, as closely as can be traced:—

$$5(NH_4SO_3)_2O + 5NH_4N(SO_2)_2O = 6NH_4HSO_4 + 3HN(SO_3NH_4)_2 + 2N_2 + NH_3 + 6SO_2 + 2SO_3.$$

This represents three-fifths of each of the pyro-salts as converted into hydrated salt, and the imidosulphonate with double as much ammonia as it had. When this change is about complete, the decomposition, at still higher temperatures, goes on in such a way as to preserve a residue nearly steady in composition as regards sulphur (29 per cent.) but to cause it to become richer in water and poorer in ammonia and imidosulphonate, until, quite at the last, the residue consists of ammonium hydrogen sulphate alone.

The result of heating 7.5 grams of the acid in an open crucible, in the way described, for eight or ten minutes, was to leave a residue crystallising in brilliant prismatic plates and weighing 4.879 grams. The loss of weight included that due to ejection of a little of the liquid as spray. The mass was analysed, and the results were calculated on the, no doubt accurate, assumption that no amidosulphonic acid could be present in it. Its composition is well represented as having three-eighths of the sulphur as imidosulphonate and five-eighths as sulphate, as follows :—

Imidosulphonates—$1NH_4N(SO_2)_2O$; $2HN(SO_3NH_4)_2$;

Sulphates—$8NH_4HSO_4$; $2(NH_4)_2SO_4$:

as the following composition shows :—

	Residue.	Total sulphur.	Sulphate sulphur.	Imidosulph. sulphur.	Ammonia nitrogen.
Calc.	65.6	28.73	17.96	10.78	13.36
Found,	65.0	28.62	17.78	10.84	13.43

These might have been derived from $28H_2NSO_3H$ by loss of $9SO_2$, $3SO_3$, $2NH_3$, $3N_2$, and it must be near the truth to say that they were. But the acid will have contained about one per cent. combined water, which will have increased the sulphate, and also made the residue,

calculated with this correction, materially greater (quite 5 per cent.); on the other hand, the heating of the acid had to be brisk, and the crucible open, or volatilised products would have been returned condensed, and this mode of working entails much more loss as spray than the number above calculated allows for. The sulphate, from this cause, being found in marked excess and the last stage of the decomposition having no doubt commenced, the results obtained are plainly in accordance with the assertion that the pyro-salts become hydrated at about the same rate, until hydration of the residue is complete.

In an experiment, where the heating was stopped when a little more than half of the acid had been rapidly driven off, the residue gave, on analysis, 29 per cent. sulphur and 14.4 nitrogen, a result which nearly corresponds to $4NH_4HSO_4$, $1HN(SO_3NH_4)_2$, and $1H_2NSO_3H$ (in form of the two pyro-salts). In another case, when only a fourth of the acid had been expelled, the liquid residue was at once decanted into a second crucible, except for a sixth of it, which had crystallised. The two portions showed a somewhat different composition; that left behind contained 28.83 per cent. sulphur, the decanted part contained 29.44 per cent. sulphur and 16.8 per cent. nitrogen as ammonia.

The ammonium salt.—The melting point of the thoroughly dry ammonium salt is 135°, as determined in a capillary tube, by a Jena thermometer with stem all immersed in the sulphuric-acid bath. The melted salt, when in some quantity, remains in fusion at temperatures as low even as 70°. Heated much above its melting point, the salt, in part, becomes imidosulphonate, at first, apparently, the isomeric normal ammonium salt, $2H_2NSO_3NH_4 = NH_4N(SO_3NH_4)_2$ ('sulphatammon'), which then, with rising temperature, changes into ammonia and the two-thirds normal salt, $HN(SO_3NH_4)_2$ ('parasulphatammon'), but yet not fully before the latter salt begins to decompose into sulphate, sulphur dioxide, and nitrogen. The phenomena observed are that

at 180° bubbles begin to form in the liquid, and enlarge and increase up to 190°, which are almost wholly reabsorbed on cooling the liquid to 130°. If the temperature is very slowly and continuously raised, effervescence of ammonia goes on equably, but if it is maintained constant, the escape of ammonia soon lessens. Having reached 240° in two hours, the liquid cooled down again begins to form tufts of silky fibres at 130°, which grow with fall of temperature, and remain enclosed in a clear vitreous mass, unchanged for days, whereas ammonium amidosulphonate cooled after having been barely fused, forms an opaque homogeneous mass of small prisms. The mass, thus cooled from 240°, weighs less than the salt taken, by nearly half the weight of the difference in ammonia between normal and two-thirds normal ammonium imidosulphonate. When heated very gradually to 310°, it still evolves ammonia slowly at that point, but other gases also, which form with the ammonia a slight pseudo-sublimate. With loss of ammonia, the solidifying point of the liquid rises, so that, on cooling slightly, solidification into a hard crystalline mass of the two-thirds normal ammonium imidosulphonate occurs. This mass is neutral, except where it has been more strongly heated in contact with glass, treatment which decomposes it, renders it acid from presence of acid sulphate, and causes it to attack the glass in a remarkable manner, so as to strongly Réaumurise it and lessen its weight considerably, without eroding it. The imidosulphonate can be tested for and roughly estimated, by dissolving the mass in water containing ammonia, cautiously concentrating the solution, and adding solid potassium chloride. The sparingly soluble potassium salt can be thus obtained, collected, and weighed. Another way is to precipitate the ammoniacal solution by barium chloride, and determine the alkalinity of the normal barium salt, as a measure of the imidosulphonic acid in it. We have succeeded in converting the amidosulphonate into two-

thirds of the full quantity of imidosulphonate. In heating the salt, access of moisture must be guarded against.

Berglund observed the production of imidosulphonate by heating ammonium, or potassium, or sodium amidosulphonate, but only in very small quantity, even in the case of the ammonium salt, which gave him much the best result. According to him, the ammonium salt melts at 125°, without decomposition, and begins to be decomposed at 150°, with escape of ammonia. Imidosulphonate is formed very slowly, and is decomposed almost at the same rate. On account of the instability of imidosulphonates, the temperature must not exceed 170°. Evidently, Berglund allowed access of moist air, for the true melting point of the salt is much higher than 125°, and ammonium imidosulphonate is a nearly stable salt, even at 357°, when it boils (*This Journal*, **6**, 55).

The potassium salt.—In our paper on *Imidosulphonates* (**6**, 62) we mentioned that potassium amidosulphonate becomes ammonia and imidosulphonate when heated, and made reference to Berglund. But, at that time, we had only seen abstract accounts of his work, and have since found that, whereas we had observed a free production of the imidosulphonate at 350°, he had got only a very small quantity indeed of it, at the temperature he employed, 160–170°.

The potassium salt melts at 212° (Jena thermometer, thread immersed), but not without partial decomposition, the liquid beginning to froth, through escape of ammonia, before its temperature reaches 220°. Berglund's observation that ammonia escapes at 160–170°, though very slowly, may be set down as due to presence of the atmosphere in his experiments, for the crystals do not change before fusion, when air is shut out. The solidifying point rises as ammonia escapes, so that at 260° the residue is solid, and remains so at 280°, potassium imidosulphonate melting only at a red heat, as found by us (*op. cit.*, p. 63). By far the greater part of the residue consists of the (neutral)

two-thirds normal potassium imidosulphonate, but there is always a marked quantity of the corresponding ammonium salt, as well as a little sulphate. Just on melting, the amidosulphonate evidently decomposes, thus :—$2H_2NSO_3K = NH_4N(SO_3K)_2$, which almost at once begins to evolve ammonia. The explanation of the production of ammonium salt and of sulphate must be the same as that in the case of the barium salt next described, but in heating the potassium salt, anything volatile but ammonia was hardly to be recognised.

The barium salt.—According to Berglund, the behaviour of the barium salt, when heated, is radically different from that of the alkali salts, for, whereas these slowly decompose at 160–170° into ammonia and imidosulphonate, which then becomes sulphate, the barium salt suffers no change up nearly to 200°, and then decomposes into sulphate, ammonia, nitrogen, and sulphur dioxide, while no imidosulphonate can be detected. But Berglund was mistaken ; there is a difference, but not a fundamental one, for imidosulphonate is formed.

Barium amidosulphonate decomposes without suffering any kind of fusion. As Berglund stated, only a little below 200° does ammonia begin to come off from it, and not till about 240° does this freely escape. At about 275°, there is production of a sublimate of orange nitrogen sulphide, a very little sulphur, a small sublimate of ammonium pyrosulphite, and, no doubt, nitrogen, along with the ammonia. Although, now, the salt looks little changed, it has lost considerably in weight (7.53 per cent., observed), and become caked. Water dissolves out of it quite a quantity of the two-thirds normal ammonium imidosulphonate. When the salt is less heated, water dissolves out of the mass a little barium imidosulphonate, as well as ammonium salt ; but after the greater heating, no soluble barium salt is left. The explosive nitrogen sulphide was quite certainly identified as such. To decompose the barium salt without

getting sulphate produced was not found possible. The mode of the formation of the sulphate may apparently be regarded as that represented by—

$$3Ba(SO_3NH_2)_2 = 3BaSO_4 + HN(SO_3NH_4)_2 + NH_3 + NS + N.$$

The hydroxylamine salt.—When sufficiently heated, this salt decomposes suddenly.

The silver salt.—Crystals of the silver salt decrepitate, when heated, and become topaz-yellow, without losing form or transparency. The melting point of this stable salt we have neglected to take, but, apparently below 200°, it melts to an opaque, viscid, yellow, and comparatively very stable liquid, probably imidosulphonate, $NH_4N(SO_3Ag)_2$. By stronger heating this liquid gives off ammonia, with frothing, and becomes semi-solid, being then probably, $HN(SO_3Ag)_2$. To decompose this, temperatures approaching a red heat are necessary; it then becomes liquid again and gives, along with more free ammonia and a little water, a white sublimate, which behaves as ammonium thiosulphate, giving much milk of sulphur and sulphur dioxide with hydrochloric acid. The residual mass, when cold, looks just like gamboge; it consists mainly of silver sulphate, but contains a little ammonium salt.

The oxymercuric salt.—The oxymercuric salt bears heat well. It gives off water freely in the first place, and when hotter becomes bright yellow, but whitens whenever cooled. Near a red heat it yields a small sublimate, then melts and freely effervesces, the gases being sulphur dioxide and nitrogen. At a red heat much mercury, as well as mercury sulphates, volatilises. The yellow liquid, on cooling, becomes a white solid, consisting essentially of sulphates. In the remarks which follow, the mercury salt is not taken into consideration, its decomposition being specific.

Summary account of the effects of heating the acid and its salts.—Varied as are the details of the decomposition of amidosulphonates by

heat, according as they concern the acid or its barium salt, the ammonium or the potassium salt, the characteristics of the decomposition are the same. Always there is, virtually, the change of two mol. amidosulphonate into imidosulphonic acid and ammonia and, for the most part, the union of these to form a normal salt :—

$$2H_2NSO\,H = NH_3 + HN(SO_3H)_2\,;\ (H_2NSO_3)_2Ba = NH_3 + HN(SO_3)_2Ba.$$

That change is the cumulative resolution of an amine ; next comes the cumulative resolution of the imidosulphonate as a hydroxide or metal-loxide. The elements of one mol. water and, in the case of metal salts, one mol. basic oxide, go from one mol. of the imidosulphonate to another mol. of it, converting this into sulphate, pyro or normal, as the case may be, and leaving either pyro-imidosulphonate as a residue, or (when basic oxide has been also lost), nitrogen, ammonia, and sulphur dioxide as representatives of what, at lower temperatures might have been sulphimide :—

$$2NH_4N(SO_3H)_2 = (NH_4SO_3)_2O + NH_4N(SO_2)_2O\,;$$
$$2NH_4N(SO_3)_2Ba = 2BaSO_4 + 2NH_3 + [2HNSO_2].$$

The complex $[2HNSO_2]$ appears as $\frac{2}{3}(NH_3 + N_2 + 3SO_2)$, or, in the case of the barium salt (infusible as that is and acquiring a higher temperature as it does), this complex partly interacts with the $2NH_3$, according to the equation :—

$$2NH_3 + 2HNSO_2 = 4OH_2 + 2NS + N_2.$$

We are indebted for their kind assistance, to Mr. Y. Osaka, B. Sc. in examining the reactions of silver amidosulphonate, and to Mr. M. Chikashige, B. Sc., in examining the compound of amidosulphonic acid with sodium sulphate.

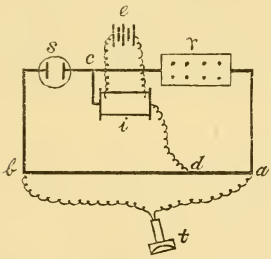
Molecular Conductivity of Amidosulphonic acid.

by

Jōji Sakurai, F.C.S., *Rigakuhakushi.*

Professor of Chemistry, College of Science, Imperial University.

At the request of Dr. Divers F.R.S., I have determined the molecular conductivity of amidosulphonic acid. The apparatus which I used for the purpose, consisted of a Kohlrausch's universal bridge, in which the measuring scale is so graduated that the index at once gives the ratio of the lengths of its arms. The essential parts of the whole arrangement are sketched out in the accompanying figure. The primary current from two Daniell's elements, *e*, enters the induction coil, *i*, the induced current divides at *c* (or *d*), one part passing through the solution, *s*, and the other through the rheostat, *r*, both to return to the coil through *d* (or *c*). *ab* is the measuring wire along which the index, *d*, is moved until the telephone, *t*, no longer speaks, at which point we have for the resistances of the various parts the following relation :—



$$s : r :: bd : ad$$

$$\text{or} \qquad s = \frac{bd}{ad} r.$$

Since the index, d, at once gives the ratio, $\frac{bd}{ad}$, the resistance of the vessel containing the solution is obtained by simply multiplying the resistance of the rheostat by this ratio. In all the determinations I so arranged the resistances that the index should always lie between 0.9 and 1.0 divisions on the scale when the telephone was silent; in this manner, any inaccuracy arising from possible errors of calibration was reduced to the minimum. This part of the scale is subdivided into ten parts, and it is easy to read to one-half of these divisions. Instead of attempting to catch the sound-minimum of the telephone, I determined the limits of the region of silence and took the arithmetical mean of these limits as the true sound-minimum, as for example, $0.955-0.975=0.965$. For each dilution I made two sets of determinations by slightly altering the resistance of the rheostat, each set consisting of two separate readings, and took the mean of these four readings.

The resistance vessel for holding the solution, which I employed, is of the Arrhenius form and was made by following the directions given by Ostwald. (*Handbuch für physiko-chemische Messungen*). Burettes and pipettes were also accurately calibrated according to the methods described in the same valuable work.

The temperature, at which the determinations were made, was 25.°00—25.°05 throughout, this constant temperature being maintained in a water thermostat worked by a small water-turbine.

Resistance capacity of the vessel. For determining the resistance capacity of the vessel, I employed $\frac{1}{50}$ N solution of potassium chloride, whose specific conductivity is accurately known to be $\lambda=2.594\times10^{-3}$, at 25°. If l=measured conductivity of the vessel containing $\frac{1}{50}$ N solution of potassium chloride and c=its resistance capacity, then—

$$c=\lambda/l.$$

The results obtained are given below, in which r=resistance of the rheostat and R=ratio of the two arms of the scale, $\frac{bd}{ad}$.

r	R (1)	R (2)	R Mean	$r.R=\frac{1}{l}$
155	.955−.975=.965	.955−.975=.965	.965	149.58
156	.95 −.97 =.96	.95 −.965=.9575	.9588	149.57
157	.94 −.965=.9525	.945−.96 =.9525	.9525	149.54
158	.935−.96 =.9475	.935−.955=.945	.9463	149.52
159	.93 −.95 =.94	.93 −.95 =.94	.94	149.46
160	.925−.945=.935	.925−.945=.935	.935	149.60
			Mean	149.55.

Hence, $c=\lambda/l=2.594\times10^{-3}\times0.14955\times10^{3}=0.387933.$

Specific conductivity of water. Taking advantage of the cold weather at the time, I purified the distilled water employed for making and diluting the solutions by freezing a portion of it. The ice formed was melted and used in all the determinations. Its specific conductivity was determined with the following results :

r	R	$r.R$
10,000	18−22=20	200,000
11,000	17−22=19.5	204,500
	Mean	202,250.

Hence, $\lambda=c.l=0.387933\times\frac{1}{202,250}=1.9\times10^{-6}.$

As the molecular conductivity of the solutions was determined for v=32, 64, 128, 256, 512, and 1024 liters, the corrections for the conductivity of water for the respective dilutions are—

δ_v=0.06, 0.12, 0.24, 0.49, 0.97, and 1.94 ;

these corrections being obtained by multiplying the specific conductivity of water, as above determined, into the molecular volume of the respective solutions, expressed in c.c. No account was taken of these corrections in the case of the molecular conductivity of amidosulphonic acid, inasmuch as the latter is of a very considerable magnitude when compared with these ; moreover, it is difficult to know whether the impurities in water increase or diminish the conductivity of the acid. In the case of the sodium salt, the above corrections were duly deducted from the measured conductivity.

Molecular conductivity of amidosulphonic acid, $NH_2SO_3H=97.11$. A $\frac{1}{32}$ N solution of the pure acid having been made by dissolving 0.1517 gr. in 50 c.c., 20 c.c. of it were transferred to the resistance vessel and, when a constant temperature of 25° had been attained, a set of conductivity observations was carried out, with changes of resistance, as already stated. Then, 10 c.c. of the solution were removed from the vessel and replaced by water, and another set of determinations made, and so on, until the strength of the solution was reduced to $\frac{1}{1024}$ N. The results are tabulated below, in which v is the molecular volume of the solution in liters, and r and R have the same meaning as before.

v	r	R (1)	R (2)	R Mean	$r.R=\frac{1}{l}$
32	44	.94 −.965=.9525	.945−.965=.955	.9538	41.97
,,	45	.915−.95 =.9325	.92 −.945=.9325	.9325	41.96
				Mean	41.97
64	80	.95−.975=.9625	.95−.975=.9625	.9625	77.00
,,	82	.93−.95 =.94	.93−.95 =.94	.94	77.08
				Mean	77.04

128	150	.955−.98 =.9675	.955−.98 =.9675	.9675	145.13
,,	152	.945−.965=.955	.945−.97 =.9575	.9563	145.36
				Mean	145.25
256	290	.945−.965=.955	.94−.965=.9525	.9538	276.60
,,	294	.925−.950=.9375	.93−.955=.9425	.94	276.36
				Mean	276.48
512	570	.95−.975=.9625	.95 −.975=.9625	.9625	548.63
,,	580	.93−.955=.9425	.935−.965=.95	.9463	548.85
				Mean	548.74
1024	1120	.955−.98 =.9675	.955−.98 =.9675	.9675	1083.60
,,	1140	.94 −.965=.9525	.93 −.97 =.95	.9512	1084.39
				Mean	1084.00.

The molecular conductivity of amidosulphonic acid for the respective dilutions, μ_v, are, therefore,—

$$\mu_{32} = 0.387933 \times 32/\ .04197 = 295.78$$
$$\mu_{64} = \quad ,, \quad \times 64/\ .07704 = 324.86$$
$$\mu_{128} = \quad ,, \quad \times 128/\ .14525 = 341.87$$
$$\mu_{256} = \quad ,, \quad \times 256/\ .27648 = 359.20$$
$$\mu_{512} = \quad ,, \quad \times 512/\ .54874 = 361.95$$
$$\mu_{1024} = \quad ,, \quad \times 1024/1.08400 = 366.46$$
$$[\mu_{\infty} = 373.97].$$

The molecular conductivity of the acid at infinite dilution, μ_{∞}, has been calculated from that of the sodium salt.

Molecular conductivity of sodium amidosulphonate. A solution of pure sodium hydroxide, prepared from metallic sodium, was made, titrated with pure and crystallised oxalic acid, and made up to $\frac{1}{32}$ N, phenol-phthalein being used as the indicator. About 30 c.c. of this

solution were carefully neutralised with powdered amidosulphonic acid with addition of a trace of phenol-phthalein, and filtered with the usual precautions. Then, 20 c.c. of the neutral solution were transferred to the resistance vessel, and conductivity determinations were made in exactly the same manner as with the acid. The results are as follows :—

v	r	R (1)	R (2)	R Mean	$r.R=\frac{1}{l}$
32	155	.945−.96 =.9525	.935−.96 =.9475	.95	147.25
„	156	.935−.955=.945	.93 −.955=.9425	.9438	147.23
				Mean	147.24
64	295	.94 −.975=.9575	.945−.97 =.9575	.9575	282.46
„	300	.925−.96 =.9425	.93 −.95 =.94	.9413	282.39
				Mean	282.43
128	570	.95 −.97 =.96	.95 −.97 =.96	.96	547.20
„	575	.945−.96 =.9525	.94 −.96 =.95	.9513	547.00
				Mean	547.10
256	1130	.94 −.96 =.95	·94 −.96 =.95	.95	1073.50
„	1140	.93 −.955=.9425	.925−.955=.94	.9413	1073.08
				Mean	1073.29
512	2200	.935−.97 =.9525	.93 −.97 =.95	.9513	2092.86
„	2240	.915−.955=.935	.915−.955=.935	.935	2094.40
				Mean	2093.63
1024	4300	.95 −.97 =.96	.94 −.97 =.955	.9575	4117.25
„	4400	.925−.95 =.9375	.925−.955=.935	.9363	4119.72
				Mean	4118.49.

The molecular conductivity of sodium amidosulphonate is, therefore,

						δ_v	μ_v
μ_{32}	=	0.387933	×	32/ .14724	= 84.31	.06	84.25
μ_{64}	=	,,	×	64/ .28243	= 87.91	.12	87.79
μ_{128}	=	,,	×	128/ .54710	= 90.76	.24	90.52
μ_{256}	=	,,	×	256/1.07329	= 92.53	.49	92.04
μ_{512}	=	,,	×	512/2.09363	= 94.87	.97	93.90
μ_{1024}	=	,,	×	1024/4.11849	= 96.45	1.94	94.51.

It may be observed that the difference $\mu_{1024}-\mu_{32}=10.26$ is of the same magnitude as that in the case of the sodium salts of all the *monobasic* acids, showing that the ions of amidosulphonic acid are H and NH_2SO_3. For calculating the molecular conductivity of sodium amidosulphonate at infinite dilution I have made use of Bredig's table (*Zeit. physik. Chem.*, **13**, 198 [1894]), which gives a more concordant result than the use of Ostwald's values.

v =	32	64	128	256	512	1024	
d_v =	14	11	8	6	4	3	
μ_v =	84.25	87.79	90.52	92.04	93.90	94.51	
μ_∞ =	98.25	98.79	98.52	98.04	97.90	97.51	Mean 98.17.

The velocity of migration of Na-ion being 49.2, that of the NH_2SO_3-ion is $98.17-49.2=48.97$; and the velocity of migration of H-ion being 325, the molecular conductivity of amidosulphonic acid at infinite dilution, μ_∞, is evidently $325+48.97=373.97$.

Discussion of the results. The velocity of migration of the anion $NH_2SO_3=48.97$ approaches those of $BrO_3=50.5$ and $F=50.8$; it is much greater than that of $IO_3=37.9$ or $H_2PO_4=33.5$, and much less than that of $Cl=70.2$, $Br=73.0$, $I=72.0$, or $NO_3=65.1$. Among the organic anions that of formic acid, $HCO_2=51.2$, is the only one which exceeds NH_2SO_3 in velocity.

The 'strength' of amidosulphonic acid may be judged of from the degree of its dissociation, $\mu_v/\mu_\infty = m$. The following table, in which 100 times this ratio is calculated, shows that amidosulphonic acid is already dissociated to the extent of 79 % in a $\frac{1}{32}$ N solution and that the degree of dissociation attains 98 % in a $\frac{1}{1024}$ N solution:

Amidosulphonic acid ($\mu_\infty = 373.97$).

$v =$	32	64	128	256	512	1024
$\mu_v =$	295.78	324.86	341.87	359.20	361.95	366.46
$100\ m =$	79.09	86.87	91.42	96.04	96.79	97.99.

Amidosulphonic acid may, therefore, be ranked among the strong mineral acids, being nearly comparable with iodic acid, as may be seen from the following numbers:—

	100 m.	
v	H,NH_2SO_3	H,IO_3
32	79.09	84.60
64	86.87	90.11
128	91.42	93.96
256	96.04	95.89
512	96.79	97.27
1024	97.99	97.55.

In its constitution, amidosulphonic acid is sulphurous acid in which the H directly combined with sulphur has been replaced by the group NH_2:

$$O_2S<^{H}_{OH} \qquad\qquad O_2S<^{NH_2}_{OH}$$

Sulphurous acid. Amidosulphonic acid.

Now, it is evident from the determinations of Ostwald (*Jour. prakt. Chem.*, **32**, 314 [1885]) and of Barth (*Zeit. physik. Chem.*,

9, 181 [1892]) that sulphurous acid, in point of electric conductivity, behaves as a monobasic acid, its ions being H and SO_3H. It is, therefore, possible to obtain a knowledge of the influence of the replacement of H by NH_2 upon the strength of the acid, by comparing together the values of $100\,m$ of sulphurous and amidosulphonic acids. Determinations of the electric conductivity of sulphurous acid, as well as of metallic sulphites, are, however, attended with considerable inaccuracy, owing to the unavoidable and rapid oxidation occuring during the determination. The following are the numbers obtained by Barth (*loc. cit.*) at 25°:—

$v=$	32	64	128	256	512	1024
Sulphurous acid H,SO_3H ...	177.5	214.9	248.5	279.0	303.3	324.7
Hyd. sod. sulphite Na,SO_3H	80.9	84.7	88.7	92.5	95.8	98.8.

The difference $\mu_{1024}-\mu_{32}$ for the sodium salt, instead of being tbout 10, is as high as 17.9, this error arising from the partial oxidaaion of the sulphite into sulphate. The numbers obtained by Barth are, therefore, admittedly too high, the higher as the solution is the more dilute. We have, therefore, no means of calculating exactly the velocity of migration of the anion, SO_3H, but it may be approximately taken to be $(80.9+14)-49.2=45.7$, 80.9 being the value of μ_{32} for the sodium salt, 14, Bredig's constant for this dilution, and 49.2, the velocity of migration of the kation, Na. The approximate molecular conductivity of sulphurous acid at infinite dilution is, therefore, $\mu_\infty=325+45.7=370.7$, and the values of $100\,\mu_v/\mu_\infty$ for this acid at the respective dilutions are—

$v=32$	64	128	256	512	1024
$100\,m=47.88$	57.97	67.04	75.26	81.82	87.59.

The increase of dissociation with dilution, as thus calculated, is admittedly too great, inasmuch as the oxidation of sulphurous acid

gives increasingly too high values of μ_v. Taking this fact into consideration and comparing the above numbers with those obtained for amidosulphonic acid—

$v=32$	64	128	256	512	1024
$100\,m=79.09$	86.87	91.42	96.04	96.79	97.99,

it becomes evident that *amidosulphonic acid is much stronger than sulphurous acid.* This conclusion, drawn from the study of the electric conductivity of amidosulphonic acid, is interesting, from the fact that the influence of the NH_2 group upon the strength of *organic* acids generally is quite of the opposite character. Thus, from the data given by Ostwald (*Zeit. physik. Chem.*, **1**, 74 [1887]), I have calculated the following values of $100\,m$ for benzene-sulphonic acid :—

$v=32$	64	128	256	512	1024
$100\,m=90.91$	93.95	96.15	98.15	99.61	100.00.

Benzene-sulphonic acid is thus one of the strongest acids, whilst its amido-derivatives are far below it in strength, as may be seen from the following numbers (Ostwald : *Zeit. physik. Chem.*, **3**, 406 [1889]) :

	100 *m*.		
v	*o*. Amidobenz. sulphon. acid.	*m*. Amidobenz. sulphon. acid.	*p*. Amidobenz. sulphon. acid.
32	—	—	12.79
64	36.6	10.25	17.52
128	47.1	14.26	23.80
256	58.5	19.70	31.80
512	69.8	26.55	41.60
1024	80.0	34.70	53.00.

Again, benzoic acid is stronger than its amido-derivatives, and acetic acid, though itself a very weak acid, is yet incomparably

stronger than glycocoll. These are facts already well established (compare J. Walker : *Proc. Chem. Soc. Lond.*, [1894]).

The striking contrast between the influence of NH_2 upon the strength of organic acids generally and that upon sulphurous acid—the only inorganic acid of which the electric conductivity of the amido-derivative has been determined—has, in all probability, to be accounted for by the circumstance that, in the former, the basic group $-R''-NH_2$ acts upon CO_2H or SO_3H, forming internal ammonium salts, as was first suggested by Erlenmeyer (compare J. Sakurai : Constitution of glycocoll and its derivatives, *Jour. Coll. Sc.*, **7**, 87 [1895]). Indeed, Ostwald, after determining the molecular conductivity of glycocoll and finding that it increases only very slightly on dilution, goes on to say : "The nature of this series of numbers is rather that of a neutral salt, and the conclusion already drawn from the neutral reaction of glycocoll that it is a salt-like compound is confirmed by the electrical measurements." (*Jour. prakt. Chem.*, **32**, 369 [1885]). In another paper, the same author speaks of amido-acetic acid as one, "which can no longer be called an acid." (*Zeit. physik. Chem.*, **3**, 189 [1889]).

I have shown in another place (*loc. cit.*) that the conclusion is inevitable, that not only glycocoll but organic amido-acids generally are salt-like compounds ; the study of the electric conductivity of amidosulphonic acid has confirmed this view by showing that mere presence of NH_2 does not diminish the strength of an acid and that the fact, therefore, that organic amido-acids are weaker than the non-amidated acids must be explained by assuming the nitrogen of the basic group, $-R''-NH_2$, to be in combination with the hydrogen of the acid group, CO_2H or SO_3H, thus :—

$$\underbrace{H_3N-R''-CO-O} \qquad \text{or} \qquad \underbrace{H_3N-R''-SO_2-O}\ ,$$

the dissociation of these molecules into H, on the one hand, and H_2N - R''-C O-O or H_2N - R''- SO_2- O, on the other, occurring to a much less extent than in the case of non-amidated acids, which dissociate into H and $R'CO_2$ or $R'SO_3$. It may be observed that the introduction of a group into organic amido-acids that diminishes their salt-like character must facilitate their dissociation, and thus increase their conductivity and strength. The superior conductivity of aceturic and hippuric acids compared with glycocoll may be cited in favour of this view.

The law of dilution. As is well known, Ostward's dilution-formula—

$$k=\frac{\left(\frac{\mu_v}{\mu_\infty}\right)^2}{\left(1-\frac{\mu_v}{\mu_\infty}\right)v},$$

which expresses the relation between conductivity, μ_v, and dilution, v, of electrolytes which are only moderately dissociated, does not apply in the case of highly dissociated electrolytes. Now, Rudolphi has shown (*Zeit. physik. Chem.*, **17**, 385 [1895]) that the following empirical formula well expresses this relation :

$$k=\frac{\left(\frac{\mu_v}{\mu_\infty}\right)^2}{\left(1-\frac{\mu_v}{\mu_\infty}\right)\sqrt{v}};$$

and, further, van't Hoff (*Zeit. physik. Chem.*, **18**, 300 [1896]) has pointed out that the relation may be equally well expressed by altering Rudolphi's formula into

$$k=\frac{\left(\frac{\mu_v}{\mu_\infty}\right)^{\frac{3}{2}}}{\left(1-\frac{\mu_v}{\mu_\infty}\right)\sqrt{v}}=\frac{\left(\frac{\mu_v}{\mu_\infty}\right)^3}{\left(1-\frac{\mu_v}{\mu_\infty}\right)^2 v}=\frac{\left(\frac{\mu_v}{\mu_\infty}\cdot\frac{1}{v}\right)^3}{\left\{\left(1-\frac{\mu_v}{\mu_\infty}\right)\frac{1}{v}\right\}^2},$$

which may be written as

$$k=\frac{c_i^3}{c_s^2},$$

where $\frac{\mu_v}{\mu_\infty}\cdot\frac{1}{v}=c_i$ is the concentration of the ion, and $\left(1-\frac{\mu_v}{\mu_\infty}\right)\frac{1}{v}=c_s$ is that of the undissociated salt. I have tested the above formulæ with sodium amidosulphonate ; the results which are tabulated below are in agreement with both of them :

Sodium amidosulphonate, $\mu_\infty=98.17$.

$v=32$	64	128	256	512	1024
$\mu_v=84.25$	87.79	90.52	92.04	93.90	94.51
$k_R=$ 1.00	1.03	1.05	0.96	1.01	0.85
$k_H=$ 1.00	1.01	1.01	0.92	0.96	0.80.

The values of k_R and k_H have been calculated according to Rudolphi's and van't Hoff's formulæ, respectively, the value found for $v=32$ liters being, in both cases, made equal to 1. The results are almost equally constant up to $v=512$ liters, but, in both cases, there is a greater deviation for the last dilution, owing, no doubt, to a greater experimental error.

The Physiological Action of Amido-sulphonic Acid.

by

Oscar Loew, Ph. D., Prof.

College of Agriculture, Imperial University.

Upon the suggestion of my colleague, Dr. Edward Divers, I have made a series of physiological tests on plants with amidosulphonic acid (amidosulphuric acid). This acid, in 0·05–0·1 per cent. solutions, was applied in the form of its calcium or sodium salt, either alone or in conjunction with mineral nutrient salts, viz.: monopotassium phosphate, 0·05 %; magnesium sulphate, 0·05 %; calcium sulphate, 0·1 %; and a trace of ferrous sulphate. These solutions (500 cc.) were applied to whole plants, or to branches and isolated leaves, of different families of the phænogams; also to algæ, lower fungi, and lower aquatic animals.

The principal result, in regard to phænogams, was that amido-sulphonic acid has, even in its salts, a *decidedly noxious action* upon them, clearly established by control experiments, made at the same time and upon similar organisms, kept in water and in solutions of ammonium sulphate and sodium sulphate. Some of the experiments were the following:—

Young wheat plants, carefully taken from the field, 20–25 cm. high, were placed in three vessels, containing each 500 cc. of (*a*) common water; (*b*) 0·1 % solution of neutral ammonium sulphate; (*c*) 0·1 % solution of sodium amidosulphonate. In (*a*) and (*b*) new rootlets

gradually developed, but not in (*c*). After five days, withering of the leaves commenced in (*c*) and complete death had happend in nine days; while the plants in (*a*) and (*b*) were still perfectly healthy.

Young branches of *Prunus Cerasus*, 40 cm. long, were placed in the same solutions and also in 0·1 per cent. of hydrated sodium sulphate. After three days, brown spots had appeared upon all the leaves kept in the amidosulphonate, and two days later all these leaves were dried up; while in the control solutions the branches still remained healthy, and for a long time afterwards.

Isolated leaves of *Æsculus* and *Morus* behaved in these solutions in the same way. Mr. Maeno made, under my supervision, further experiments with young plants of *Allium fistulosum*, *Soja hispida*, and *Brassica Rapa*, and in all these cases some noxious action of calcium amidosulphonate became evident. In these experiments all the mineral nutrients were present.

In contrast to what precedes, algæ (*Spirogyra*, *Mesocarpus*) had not suffered even in 1 per cent. solution of calcium amidosulphonate, after a week; while the ammonium salt killed them in 0·5 per cent. solution, within two days.*

That mould-fungi and bacteria can utilise amidosulphonic acid as a source of nitrogen was clearly established by their development in solutions containing 1% cane-sugar; 0·1% monopotassium phosphate; 0·01% magnesium sulphate; and, as the only source of nitrogen, 0·1% amidosulphonic acid, either free or as calcium salt. Mr. Maeno studied the matter closely with beer-yeast, and observed that, although the acid can be utilised as a source of nitrogen, it is not so good for the purpose as ammonium sulphate. 10 cc. of thin beer-yeast, corresponding to 0·0613 gram dry matter, were suspended in a

* All ammonium salts are, for these kinds of algæ, noxious in this concentration.

solution containing in 100 cc., 6·856 grams glucose, 0·1 gram magnesium sulphate, 0·2 gram monopotassium phosphate, and 0·1 gram sodium amidosulphonate (A). In a second flask (B), the last mentioned salt was replaced by 0·1 gram ammonium sulphate. After five days, the yeast in (A) had increased 169 per cent. and that in (B) 223 per cent.; while of the glucose there had been fermented in (A) 48·8 per cent. and in (B) 55·2 per cent.

Finally, it may be mentioned that upon lower aquatic animals, as infusoria, rotatoria, and copepoda, calcium amidosulphonate, in 0·1 per cent. solution, had no noxious action.

The poisonous action of amidosulphonic acid upon phænogams is of considerable interest. Ammonia, in its salts, acts, noxiously also, but only in higher concentration ; it is never stored up as such in plants, as nitrates are, but is quickly converted into an indifferent substance, *asparagine*, as the recent investigations of Kinoshita and Suzuki, in the College of Agriculture, Tōkyō, have placed beyond doubt. It is failure of the plants to convert amidosulphonic acid into an analogous indifferent substance, that perhaps, gives time for the gradual action of the labile amido-group upon the living protoplasm. The poisonous action of the labile amido-groups in hydroxylamine and diamidogen for the most varied organisms is well known.

The fact that amidosulphonates are poisonous neither for lower plants, like algæ and low fungi, nor for animals (see the ADDENDA to this paper) still needs an explanation that shall be perfectly satisfactory. The corresponding carbamic acid was found by Nencki to have poisonous properties for animals.

ADDENDA, BY EDWARD DIVERS. Further experiments upon the physiological action of amidosulphonic acid are in progress in Dr. Loew's laboratory in the College of Agriculture at the University, the results of which will appear in the *Bulletin* of that college. When the above paper was written, the fact had not been ascertained that amidosulphonic acid acts as a reducing agent upon alkaline silver solutions, apparently becoming oxidised into water, nitrogen, and sulphite (this vol., p. 234). This reducing power brings it into association with hydroxylamine, hydrazine, and amidogen, which Dr. Loew has shown to be so highly poisonous; though only remotely, because its reducing power is so feeble compared with theirs. The simultaneous generation of sulphite should add to its poisonous action.

PROF. D. TAKAHASHI, of the College of Medicine of this University has examined the action of sodium amidosulphonate upon vertebrate animals, and has kindly communicated his results to me. He injected 0·2 gram of it subcutaneously into a frog, and intravenously 1·4 grams into a young dog, weighing 2 kilogr., in both cases without any injurious effect or any symptoms like those observed by Nencki in experiments with sodium carbamate. Amidosulphonates are, therefore, not poisonous to animals.

The Reduction of Nitrososulphates.

by

Edward Divers, M. D., F. R. S., Prof.

and

Tamemasa Haga, F.C.S., *Rigakuhakushi,* late Asst. Prof.

College of Science, Imperial University.

In 1885 (*J. Ch. Soc.*, **47**, 203) we studied the action of sodium amalgam upon a solution of potassium nitrososulphate, and found that it produced sodium hyponitrite and sulphite, besides nitrous oxide, hydroxylamine, and ammonia. In 1894 Duden (*Berichte*, **27**, 3498) examined this action, in order to see whether hydrazine was not also produced, and found that it was, in small quantity. This interesting result has caused us to re-examine this action, with the object of ascertaining whether what we had judged to be hydroxylamine is not hydrazine. For, at the time of our former work, hydrazine had not been discovered, and this substance would have given us the reactions upon which we relied as evidence of the presence of hydroxylamine. We felt it also desirable to see whether this or hydrazine was the strongly reducing substance which, in very small proportion, accompanies the hyponitrite formed from a nitrite by the action of sodium. The results of our investigation have not only cleared up these two points, but have shown that, besides hyponitrite and nitrous oxide, sulphite, hydrazine, and ammonia, there is also a large production of sulphate and amidosulphonate. Before treating of these results, we

have some experience to report concerning the preparation of potassium nitrososulphate, that may be useful.

Preparation of potassium nitrososulphate.—It is a mistake to suppose that nitric oxide is slow to unite with potassium sulphite; it is only the insolubility of nitric oxide in water that retards the union, as the use of suitably shaped vessels shows. We have had made for us four strongly flattened conical bottles, and have connected them in series by means of corks and tubes. The diameter of the flat bottom of the bottles is, on the inside, 19·5 cm., while their inside height up to the commencement of their neck is, axially, only 3 cm. With 100 cc. of solution in one of them, there is a depth of only 3–4 mm. and a free surface of nearly 300 sq. cm. The four bottles together give, therefore, a surface of 1200 sq. cm. to 400 cc. of solution, further increased by the circumstance that the salt, as it forms, grows up in small heaps above its level. A concentrated solution, such as that containing 40 per cent. potassium sulphite and 5 per cent. potassium hydroxide, will give a yield of crystals weighing 70 grams or more in 3 hours. In cold or temperate seasons, external cooling is of little use; motion of the bottles, beyond an occasional tilting, is also uncalled for. Replacement of air at the beginning, and of nitric oxide at the finish, by hydrogen is, of course, necessary, but the production of a very little oximidosulphonate or nitrite is hardly of moment, since these remain in solution. The salt when drained on tiles is pure enough for most purposes. For special work, like the present, it can be purified and got in good crystals by dissolving it quickly in 4–5 times its weight of water at 50–60°, containing 1–1·5 per cent. of potassium hydroxide, but not without considerable loss.

Process of reduction by sodium amalgam.—The amount of water present with the salt seems to be without effect on the course of the reduction; the extremes we have used have been from 3 to 10 parts

water to 1 part salt. To the water has been added, at starting, 1 per cent. of its weight of sodium hydroxide, as a precaution. When much less than 10 parts of alkaline water are taken, some of the salt remains undissolved during the earlier stages. From this cause, less than 3 parts water are insufficient. The amalgam we used was one of about $2\frac{1}{2}$ per cent. sodium. The reduction goes on rapidly at the common temperature and is attended with much heating. If the nitrososulphate solution is cooled below 0°, sodium amalgam acts upon it only when it first comes in contact with it ; perhaps, it would not even then, if it itself were first cooled down. At this low temperature, action is arrested for any period ; but soon after the vessel is removed from its bath, action sets up and, once started, is not easily checked by returning the vessel to the bath, the solution being kept warm by its interaction with the sodium. A moderate rise of temperature, up to 40°, for instance, does not seem to lessen the production of either hydrazine or hyponitrite, or to affect their preservation. The sodium requisite to reduce the nitrososulphate is, as nearly as could be estimated, $3Na : K_2N_2SO_6$; but to destroy all the hydrazine much more is required (we used 2 Na additional for this purpose). After the main change is complete, the interaction between amalgam and solution is very slow ; the solution remains cold, and hydrogen makes its appearance, along with much ammonia. The contact of amalgam with the solution has been maintained in our experiments for 24 hours, or for 2 days ; but, with continuous shaking during the second stage, much less time would have sufficed. We used a stoppered vessel, the loose stopper acting effectively as a valve in keeping air out.

Hydroxylamine a product of the reduction of a nitrite by sodium amalgam.—The testing for a small quantity of hydroxylamine, alone or in presence of hydrazine, possessing some novelty, it is well to describe the positive result in the case of sodium nitrite, before the negative

one with potassium nitrososulphate. The process we adopted consisted in shaking the solution with acetone, distilling with steam to get over the acetoxime, and evaporating the distillate with hydrochloric acid, in order to get the hydroxylamine as its hydrochloride. Concerning the formation of acetoxime, we have to remark that when we left the acetone with the solution made neutral to litmus, so as to have the hydroxylamine free but no alkali present, the formation of the acetoxime was very slow and unsatisfactory, but that it was quickly completed when we had potassium hydroxide present in some quantity. In distilling the strongly saline solution by steam, we superheated the steam. Having proved the absence of hydrazine in the product of the action of sodium amalgam upon a solution of sodium nitrite, we were able in the above way to get crystals of hydroxylamine hydrochloride from it.

Hydroxylamine not a product of the reduction of nitrososulphate by sodium.—After removing hydrazine from the solution of reduced nitrososulphate by means of benzaldehyde and ether, and evaporating residual ether, we tested for hydroxylamine by the acetone method, and failed to find any. Besides, with removal of hydrazine, all reducing power upon cupric oxide disappeared from the solution.

Hydrazine.—Hydrazine is quickly formed from nitrososulphate by sodium amalgam, and is then slowly decomposed by it. So long as any nitrososulphate remains, the action of the sodium is diverted from the hydrazine.

Ammonia can hardly be ranked as a product of the reduction of nitrososulphate, being the result of the hydrogenisation of the hydrazine. During the reduction proper, it is almost entirely absent, but makes its appearance in quantity when the sodium is able to act upon the water and liberate hydrogen.

Hyponitrite.—The hyponitrite produced by the reduction of

nitrososulphate is unstable and continuously decomposes in its alkaline solution, with evolution of gas. After treating nitrososulphate for only 24 hours with sodium, the solution was mixed with excess of barium nitrate and filtered from the precipitate produced. Silver nitrate and some nitric acid added to the filtrate precipitated first a little reduced silver and then silver hyponitrite equivalent to almost a fifth of the total nitrogen of the nitrososulphate.

Nitrous oxide and nitrogen.—No estimate has been attempted of the nitrous oxide, but it is formed, certainly, in large quantity. It appears to be generated along with amidosulphonic acid, as well as with hyponitrite. Nitrogen probably accompanies it, since hydrazine is produced.

Sulphate.—There being so much sulphite produced we expected difficulty in determining whether sulphate was a direct product of the reduction of the nitrososulphate, or only the result of incidental oxidation of sulphite by the air. But we experienced none. When the water present is not more than 3 parts to 1 of nitrososulphate, anhydrous sodium sulphate precipitates out before the solution has been removed from the amalgam and come in contact with air. We have got, in this way, 4 grams of anhydrous sodium sulphate (containing only a very little sulphite) from 50 grams of potassium nitrososulphate. Not much sulphate then remained in solution, for the barium precipitate from it largely dissolved in hydrochloric acid. It must be remembered that in concentrated solutions of alkali, salts are very little soluble. It would seem safe to say that as much as one-seventh of the sulphur is yielded by the reduction as sulphate. The quantitative determination of the sulphate produced by the reduction is not only interfered with by the presence of sulphite, but by that of much amidosulphonate; for this greatly retards, if it does not even prevent, precipitation of barium sulphate and sulphite, unless excess of barium nitrate is used,

and the solution largely diluted. In the cold, barium nitrate in bare excess, precipitates 43 per cent. of the sulphur as (very impure) sulphate and sulphite, the estimation being based on the quantity of barium nitrate used, not upon that of the precipitate. When from the acidified solution sulphur dioxide is rapidly blown out by a current of air, the precipitate, obtained by bare excess of barium nitrate, shows by its weight, after purification, that 12½ per cent. of the sulphur is obtained as sulphate. But whether sulphur dioxide has been expelled or not, and whether the solution is alkaline, neutral, or acid, the standing with more barium nitrate gives much more sulphate, and, after removal of amidosulphonic acid by mercuric nitrate, still more barium sulphate slowly deposits. The sulphate later precipitated is not formed by hydrolysis of some compound, for that would be accompanied with acidification, whereas a neutral solution depositing sulphate remains neutral. The difficulties due to the presence of amidosulphonate, as well as sulphite, are, no doubt, not insuperable, but, for the present, we are not prepared with a closely approximate determination of the quantity of sulphate present. We can assert that it is produced in a quantity between the limits of 12 and 20 per cent. of the total sulphur, an important fact enough.

Sulphite.—We have measured by iodine the sulphite formed in the reduction of the nitrososulphate, and found it equal to 31 per cent. of the sulphur. The actual determination gave no difficulty, but the previous neutralisation with so much dilute sulphuric acid as was necessary, and the other unavoidable slight exposure to air in preparing the solution, must have reduced the quantity of sulphite, and it would be unjustifiable refinement to assert more than that about one-third of the sulphur becomes sulphite. Hydrazine acts slowly upon iodine solution, but the solution used for the determination had been deprived of all hydrazine by prolonged treatment with the amalgam. Accord-

ing to the contents of the first note by one of us to the Royal Society on the *Formation of salts of nitrous oxide*, the presence of hyponitrite should have interfered, but thanks to Thum's valuable contribution (1894) to the knowledge of hyponitrous acid, in which it is correctly pointed out that hyponitrous acid does not act upon iodine (evidence to the contrary having been due to presence of acid silver hyponitrite in the crude solution), we had learned that it was without influence. In titrating, the solution was poured at once into the iodine solution, and the excess of this measured by sodium thiosulphate. One other point about the sulphite is that, after precipitating from the alkaline solution sulphate and sulphite by barium nitrate in bare excess, the solution, with more barium nitrate added to it, continued, for a day or two, to deposit barium sulphite, as well as the sulphate already mentioned.

Amidosulphonate.—The sulphur not precipitated by barium nitrate remains in solution as amidosulphonate. The precipitate also contains some amidosulphonate, although its barium salt is soluble in water. This can be extracted from the precipitate by washing it with water. Having added a small excess of barium nitrate and filtered off the precipitate, after two or three days standing, the mother-liquor, slightly acidified with nitric acid, is poured into a moderate excess of mercuric nitrate solution, in order to precipitate oxymercuric amidosulphonate (see our paper on *Amidosulphonic acid*, this vol., p. 242). This is collected and washed, and decomposed by hydrogen sulphide. The mercuric sulphide requires much washing in order to extract all amidosulphonic acid from it. The filtrate and washings evaporated to dryness in a desiccator, leave the acid in an impure form, but it can be purified, without much loss, by washing it with dilute sulphuric acid. Another way of examining the mercury precipitate is to boil it with hydrochloric acid and potassium chlorate, or to hydrolyse it at 150°, and then precipitate sulphate by barium chloride. By working in these

ways, we have ascertained the amount of amidosulphonic acid to be equal to nearly half the sulphur of the nitrososulphate.

Collection and analysis of results.—Not less than essentially three independent equations will serve to express the results of the interaction of sodium amalgam with potassium nitrososulphate. For convenience, we write these equations as four, namely,—

$$3\,[2K_2N_2SO_5+8Na+7OH_2=2H_2NSO_3K+N_2O+2KOH+8NaOH];$$

$$4\,[K_2N_2SO_5+2Na \qquad =(NaON)_2+K_2SO_3];$$

$$2\left[\begin{array}{l} K_2N_2SO_5+2Na+\ OH_2=K_2SO_4+N_2+2NaOH; \\ K_2N_2SO_5+6Na+5OH_2=K_2SO_4+(NH_2)_2+6NaOH \end{array}\right].$$

If these reactions do occur and in the proportions indicated by the numbers prefixed to them, the products will correspond in their proportions to those found, namely; amidosulphonate equal to half the sulphur and one-fourth of the nitrogen; one-third of the nitrogen as hyponitrite (three-fifths of this secured as such, before further decomposition); one-third of the sulphur as sulphite; and one-sixth of the sulphur as sulphate; together with one-sixth of the nitrogen, partly as hydrazine, partly as elemental nitrogen; and one-fourth of the nitrogen as nitrous oxide (besides that from the hyponitrite reaction), these being as yet unmeasured. Further, the above reactions in the proportions marked, represent one molecule of the nitrososulphate as being acted upon by sodium of the mean proportion of 3—$3\frac{1}{3}$ atoms, according to the relative quantities of hydrazine and nitrogen produced, a result which agrees well with observation.

Theoretical considerations.—The cause of the variety and number of the products of the reduction of a nitrososulphate by sodium is, undoubtedly, to be found in the different points at which fission of the molecule of the salt must so easily occur, as shown by the formula we have deduced for it. Under the action of sodium the salt shows the

same disposition to give both sulphite and sulphate that it does when heated and when moistened. Hitherto, it has been possible to say of the latter changes that, supposing the salt to be a sulphonate, it might give a sulphate by an oxidising process. But the present observation of the generation of much sulphate by sodium, in strongly alkaline solution, affords another proof of the impossibility of regarding a nitrososulphate as a sulphonic compound. For sodium to produce a sulphate out of a sulphite seems beyond belief. Nevertheless, Duden, having adopted for potassium nitrososulphate the constitution given it by Raschig, has not hesitated to derive a sulphate from it by the action of sodium, in an equation framed to express the formation of hydrazine. Raschig's formula is $ON{\cdot}N\begin{cases}OK\\SO_3K\end{cases}$, and is one well suited to explain the decomposition of the salt into sulphate and nitrous oxide,—too well suited, indeed, for it is hardly conceivable how, with such a constitution, a nitrososulphate could exist at all, and, if existing, could ever give back sulphite when heated. To believe that sodium amalgam would act upon a salt thus constituted, in such a way as to produce a sulphate, requires of us to go against what we know to be true of every other sulphonate. Duden detaches the OK as potassium hydroxide and then, armed with this alkali, puts its hydrogen in the place of the SO_3K and gets sulphate out of this and the OK. But there is not a case to be found of an organic sulphonate, in reaction with potassium hydroxide, yielding a sulphate instead of a sulphite. So with the sulphonated hydroxylamines, both of which decompose in concentrated potassium hydroxide solution, for they, too, give potassium sulphite. When Duden obtained hydrazine from a nitrososulphate, he furnished another proof that the salt is not a sulphonate.

There is a fact, which we have not yet brought forward in

support of the non-sulphonic constitution of nitrososulphates, that we may now give account of in this connection. It is that sodium amalgam is without action upon a true amine sulphonate or hydroxylamine sulphonate, as such. We have, indeed, just been showing in this paper that amidosulphonic acid is producible by sodium; it and imidosulphonate (no doubt, also nitrilosulphonate) are entirely unaffected by it. Oxyamidosulphonic acid in alkaline solution is also untouched by it, and in acid or neutral solution is only reduced to amidosulphonic acid (see our paper on this acid, this vol., p. 222). Schatzmann is stated by Hantzsch and Semple (*Berichte*, 1895, **28**, 2745) to have found Fremy's potassium *sulphazilate* to be reducible by sodium, but only back to the oximidosulphonate from which by oxidation it is prepared; as a sulphonate, it is not affected. Since then all amine sulphonates, oxygenated or otherwise, resist, as sulphonates, the action of sodium amalgam, while a nitrososulphate at once yields to it, the latter is not of the same class as they, that is, is not a sulphonate.

A similar point against nitrososulphates being sulphonic has been made out by Lachmann and Thiele (*Ann.* 1895, **288**, 267). It is that, whereas all undoubted sulphonic derivatives of ammonia give pure nitrous oxide, in the cold, when mixed with nitric and sulphuric acids (*cf.* Divers and Haga, *this Journ.*, 1892, **6**, 77; 1896, **9**, 233) and sometimes even a little nitramide, potassium nitrososulphate does not.

We come now to the formation of amidosulphonate, which is, essentially, that of the reduction of a sulphate to the corresponding sulphite, something, hitherto, unknown to occur, even in alkaline solution. But we have here to do with a sulphate of the group, N_2OK, and it would seem that, just as $EtSO_3K$ and $AgSO_3K$ do not oxidise to sulphate, while KSO_3K does, because it has the oxidisable potassium atom and they have a non-oxidisable atom, either ethyl or

silver; so, conversely, nitrososulphate is reducible to a virtual sulphite, because it is the sulphate of a hydrogenisable radical, whereas other sulphates have radicals, metal, alkyl, or ammonium, which do not hydrogenise. If it stood alone, the conversion of nitrososulphate into amidosulphonate might point to a sulphonic constitution for it; but other reactions make the acceptance of this impossible, unless, indeed, it could be a half sulphonic and half sulphatic salt, which seems also impossible. Were it of sulphonic constitution, it ought to yield by reduction a hydrazine-sulphonate, none of which can be found. When, after reduction, the solution is acidified and all sulphur dioxide blown out of it, it yields up all its hydrazine to benzaldehyde, and retains no discoverable hydrazine derivative.

The formation of hydrazine presents a difficulty, whatever constitution is given to the nitrososulphates, in the reduction it requires of the KON group. That this group can resist the attack of sodium amalgam is shown by the formation of the hyponitrite from a nitrite and from a nitrososulphate. Besides this, Dunstan and Dymond (*J. Ch. Soc.*, 1887, **51**, 567) specially tested the matter, and found a hyponitrite to be irreducible by sodium amalgam. Two ways out of the difficulty present themselves. It may be admitted that the group, KON_2, detached when the sodium forms alkali sulphate, is reducible to hydrazine and potassium hydroxide, although $(KON)_2$ is not. Or, considering that a nitrososulphate reverts, when heated, to sulphite and nitric oxide, even in its strongly alkaline solution, as we have shown (1895, this vol., p. 16) in the case of the sodium salt, we may assume that, to a slight extent, this reversion occurs during the heating caused by the action of the sodium amalgam, and gives nitric oxide or, rather, dinitrosyl $(NO)_2$, ready to be reduced by the sodium and water into hydrazine. In studying the action of alcohol on nitrososulphates, we have already had reason to recognise this possibility of

slight reversion occurring at the ordinary temperature, to account for the production of a little aldehyde (this vol., p. 23).

It was shown by us (1895, this vol., p. 19) that potassium nitrososulphate decomposes more slowly when dissolved in aqueous alcohol than in water, and that from the salt and the alcohol there are formed potassium hydroxide and potassium ethylsulphate, besides nitrous oxide, potassium sulphate, and a very little aldehyde. In a cold saturated solution of the salt in 23 per cent. spirit, about 14 per cent. of the salt, it was then stated, interacted with the alcohol in this way, the rest decomposing into potassium sulphate and nitrous oxide, as usual. Another experiment, in which 14 per cent. spirit was used, seemed to indicate that weaker spirit was more effective than stronger in forming alkali and ethylsulphate, but the experiment was quantitatively incomplete. We have since ascertained the effect of using 15 per cent., 5 per cent., and 2·5 per cent. spirit, estimating in each case, as before, the extent to which the alcohol had been active, by titrating the potassium hydroxide. With 15 per cent. spirit, 10·8 per cent. of the salt interacted with the alcohol; with 5 per cent. spirit, only 4·8 per cent., and with 2·5 per cent. spirit, less than 1 per cent. of the salt. Evidently, therefore, water lessens the power of the alcohol to form potassium ethyl sulphate.

Luxmoore (*J. Ch. Soc.*, 1895, **67**, 1021) has opportunely shown that a thermometer, with its bulb imbedded in potassium nitrososulphate subjected to heat, marks 127° to 148°, according to circumstances, at the temperature at which the salt explodes; for this observation agrees with Pélouze's statement that it does so at about 130°, which was the only part of his description we had failed to adequately justify. We had ascertained that the medium (air, oil), surrounding the salt, needed to be only from 91° to 108°, according to circumstances, to bring about the explosion, and it has now been established

by Luxmoore that then the salt rises of itself to about 130° before it explodes.

By the above observation, Luxmoore has cleared away a difficulty in Pélouze's description of the nitrososulphates, but has raised another, without, in our judgment, having reason for so doing. Because he has found the salt to lose $2\frac{1}{2}$ per cent. in five minutes, when at a temperature a little below 105°, he considers it impossible to explain how Pélouze could have found it not to lose weight at all. But the rate of loss varies greatly. In another of his experiments, it was little more than half as fast as the rate just quoted ; while our observation had shown that the loss need be only, 10 per cent. in $2\frac{1}{4}$ hours, and this seems to explain how Pélouze might have failed to notice sufficient loss to be deemed worth recording. We have only to assume that he exposed his salt to heat for only a short time and in a very dry atmosphere, and that he attributed the slight loss, that, even then, must have occurred, to the presence of a little moisture in his salt, as prepared. No doubt, the salt loses weight rapidly when heated in ordinary damp air ; in such air it slowly loses weight even at the common temperature, while the sodium salt does so rapidly. But in a *well-dried* atmosphere, either of air or hydrogen, as in our experiments was used, the well-dried powdered salt loses weight much more slowly ; so that it becomes probable that, with absolute dryness of salt and atmosphere, there would be no loss at all. It is surely on account of dampness of the salt, that the rate of loss is most rapid at first, as Luxmoore rightly observed ; and we must therefore, also, assume that Pélouze worked upon a well desiccated salt.

In concluding this paper, we would call attention to the small part which Sir Humphry Davy had in the discovery of the nitrososulphates, so small that we must demur to the custom, which prevails, of naming him as their discoverer, as being an injustice to the

memory of Pélouze. In the year 1800, thirty-five years before Pélouze published his work on these salts, Davy made known that, apparently, a combination of nitrous oxide with potash was obtainable by subjecting a mixture of potassium-hydroxide and sulphite, in the solid state, to the prolonged action of nitric oxide, dissolving the product in water, crystallising out potassium sulphate, and evaporating the mother liquor to dryness. The residue was a mass, which, when heated, yielded about a fourth of its weight of pure nitrous oxide. There can be no doubt that he had obtained potassium nitrososulphate, but there can be no doubt, also, that he did not know it, did not isolate the salt, and that he thought the product to be potassium *hyponitrite*, formed from nascent nitrous oxide, the nitric oxide taken having been deoxidised by the sulphite. It was Davy's observation that led Pélouze to investigate what the action really was, and to the discovery of the nitrososulphates; but that is all that Davy had to do with the discovery.

Economic Preparation of Hydroxylamine Sulphate.

by

Edward Divers, M.D., F.R.S., Prof.

and

Tamemasa Haga, F.C.S., *Rigakuhakushi,* **late Asst. Prof.**

College of Science, Imperial University.

In 1887 Raschig made known that hydroxylamine can be got from a nitrite by sulphonation followed by hydrolysis, and took out patents for its manufacture in this way. As to what extent these patents may have since been worked, and with what success, we have no information ; but we cannot believe that this process has been advantageously carried out without great modification of the directions given. The one we are about to describe is very productive and economical for the preparation of hydroxylamine sulphate, a non-deliquescent salt, readily forming large crystals, and soluble in three-quarters of its weight of water at 20°.

Commercial sodium nitrite of 95 per cent. purity does not contain more than one per cent. of objectionable matters, such as chloride and nitrate, and is, therefore, pure enough. A concentrated solution of this salt (2 mol.) and of sodium carbonate (1 mol.) pretty closely adjusted in their proportions, is treated with sulphur dioxide till just acid, while it is kept well agitated at 2–3° below zero by immersion in ice and brine. At this temperature, the conversion of the nitrite into oximidosulphonate is apparently perfect. Gently warmed with a few drops of sulphuric acid the oximidosulphonate rapidly hydrolyses,

with marked rise of temperature, into oxyamidosulphonate and acid sulphate. The solution of these salts is kept at 90–95° for two days, by the end of which time, all oxyamidosulphonate will have hydrolysed into hydroxylamine sulphate and sodium acid sulphate, while so small a quantity of ammonium salt is produced, as can only be detected in the very last mother-liquors of crystallisation by chloroplatinic acid (potassium hydroxide being an unsuitable reagent in presence of hydroxylamine). At 80–85°, five days are necessary, but then practically no ammonia is formed; at 70°, three weeks, at least, are necessary; while, at the common temperature, much oxyamidosulphonic acid remains after several months, even when much sulphuric acid has been added. On the other hand, the solution kept boiling needs seven or eight hours usually to deprive it of all sulphonate; but the boiling has disastrous effects on the hydroxylamine, destroying at east one-third of it, by converting it (through amidosulphonic acid ?) into ammonia, and wasting another third as a practically inseparable mixture of its sulphate with ammonium sulphate.

To be assured of the disappearance of all sulphonate, it is well to add barium chloride in excess to a little of the solution and filter, and then boil the filtrate with potassium chlorate, which will change any sulphonate into sulphate. Sulphonation complete, the solution is neutralised with sodium carbonate using methyl orange as indicator, and evaporated till it weighs only 10½ to 11 times as much as the sodium nitrite taken. Left to cool where its temperature will fall to 0° or lower, nearly all its sodium sulphate will crystallise out. The mother-liquor evaporated sufficiently and cooled to the common temperature yields much hydroxylamine sulphate, the mother-liquor from which, very slightly diluted and cooled below 0°, gives again a little sodium sulphate, and can be worked for more hydroxylamine sulphate, as before.

The crude hydroxylamine sulphate weighs about 9 parts for every 10 parts of sodium nitrite taken. It needs to be recrystallised, but the mother-liquors can be closely worked up. On the other hand, the sodium sulphate recrystallised, or even washed with ice-water will give up 1 part more of hydroxylamine sulphate; so that sodium nitrite will yield, on the small scale, nearly its own weight of pure hydroxylamine sulphate. No doubt, on the large scale, the theoretical yield of 118·84 per cent. could be more nearly approached.

Potassium nitrite is not well fitted for the preparation of hydroxylamine, because of the difficulty experienced in closely separating its sulphate from that of potassium. After several recrystallisations, the hydroxylamine salt contains 1·8 per cent. of potassium sulphate. The addition of aluminium sulphate is not an improvement, for then the hydroxylamine sulphate, separated as far as practicable from the potassium alum, leaves behind on ignition as much as 5·7 per cent. residue.

On the Time-Lag in the Magnetisation of Iron.

By

Yoshijiro Kato, *Rigakushi.*

With Plates VII—XV.

Preliminary Remarks.

A piece of soft iron, subjected to a change in the weak magnetic field in which it has been exposed, does not obtain its magnetic state corresponding to the change at once. When the intensity of the field is increased, a certain immediate increase in the magnetisation is apparent, but after that the magnetisation increases gradually, if the intensity of the field is kept constant. A quite similar but contrary effect is produced when the intensity of the field is decreased. This fact has been observed long since by several physicists (see Wiedemann's *Electricität*, IV, p. 236.), most of whom thought, however, that it was rather more due to the action of induced currents, than to the condition of the iron itself. A different view was taken by Prof. Ewing, F. R. S., who made a careful investigation[1] of this time-lag in magnetisation, as the phenomenon is called.

He took a piece of soft iron in the form of a wire 4 mm. thick, and starting every time from the magnetically neutral state, he applied small magnetic forces, and determined the amount of "creeping" of the magnetisation. The greatest magnetising force he used was only 0·34 C.G.S. He also tried the effect of increasing the magnetising force by a small step, when the iron was kept under the influence of a

1 *Proc. Royal Society*, **46**, p. 269 (1889).

constant field. He found that when the intensity of field, in which the specimen was kept before the step was made, was great, the time effect became conspicuous, so that when the magnetising force was 4 C.G.S., the time effect after 1 minute might be six or seven times as great as the immediate effect. He also found that when the piece of soft iron was exposed to the action of a constant magnetising force for a long time, the amount of creeping became less in comparison with the immediate effect of the step. He remarks that the amount of creeping much depends on the annealing of the specimen, and, further, that, when the iron is hardened by stretching it beyond its elastic limit, the amount of creeping becomes considerably less. In steel, whether annealed or in its usual temper, he found the creeping to be even less than in hard iron. He adds the important remark that the diameter of the wire has a great influence on the amount of creeping, the latter being less marked in thin wires. A bundle of fine iron wires bound together gave a creeping which was almost negligible in comparison with that of a solid rod of the same aggregate diameter. (It is true that this fact was observed by many experimenters before Ewing, for instance, by v. Helmholtz,[1] but it was Ewing who made it conspicuous that the phenomenon may be observed in the time-lag in magnetisation itself, apart from the effect due to the Foucault current.)

Another investigation on this subject has been made by Dr. J. Hopkinson and B. Hopkinson,[2] though in a different manner. They took a bundle of fine wires, of soft iron and hard steel, well insulated from one another, and formed them into a ring, which they subjected to the influence of a rapidly reversing magnetic field. Their conclusion is not very definite, but amounts to this that up to a frequency of

1 *Pogg. Ann.* **83**, p. 535 (1851)
2 *The Electrician*, **29**, p. 510 (1892.)

about 125 per second, the magnetic cycle is unaffected by the frequency so far as the maximum induction for a given magnetising force is concerned ; but that there is a sensible difference between the curves as determined by a slow cycle and a rapid one, most apparent in that part of the curve preceding the maximum induction ; and that this difference possibly arises from something peculiar to experiments with the ballistic galvanometer.

Dr. J. Hopkinson with his two co-workers continued the investigation,[1] and examined hard steel particularly, fully subjecting it to reversing fields of frequencies, 5, 72, 125 times per second. Their conclusions are : — " 1) As Prof. Ewing has already observed, after sudden change of magnetising force, the induction does not at once attain to its full value, but there is a slight increase going on for some seconds. 2) The small difference between the ballistic curve of magnetisation with complete cycles and the curve determined with a considerable frequency, which has already been observed, is a true time effect, the difference being greater between a frequency of 72 per second and 5 per second than between 5 per second and the ballistic curve."[2]

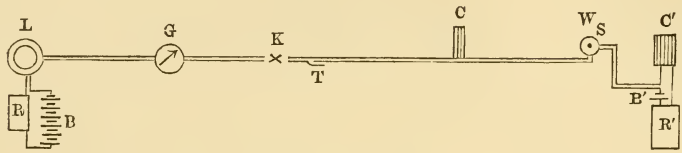
As the subject seemed to be interesting, I undertook to examine the phenomenon myself and sought to obtain some information about its nature.

Arrangement of Apparatus.

My plan was to follow Prof. Ewing's method of using an ordinary magnetometer, and observing the creeping, the only difference being that the magnetising forces were greater than were tried by him, and

1 *Proc. Royal Society*, 53, p. 352 (1893.)
2 *Loc. cit.*, p. 358.

that the wires were subjected to moderate loads. My apparatus was essentially the same as that used by him, but for the sake of clearness I may represent its arrangement.



Here, W, the specimen to be tested, is an ordinary soft iron wire, 54.86 cm. long and 2.39 mm. thick, so that its sectional area is 4.49 sq. mm. To its ends brass pieces of special form are soldered, which allow the wire to be hung in a given position and a given load to be applied to it without disturbance.

S, the magnetising solenoid, is wound on a straight brass tube, 1.2 mm. in external diameter, and consists of two sets of coils. The inner coil is put in series with a gravity Daniell cell, B′, a resistance box, R′, and a circular coil wound on a wooden reel, C′. The strength of the current is so adjusted that the magnetic field inside the coil is just equal and opposite to the vertical component of the earth's field, while the direct action of the solenoid itself on the magnetometer is compensated by the coil, C′, being placed at a suitable distance. The outer coil consists of 2590 turns of a fine copper wire, and serves for producing the magnetising fields we wish to have. The length of the solenoid is 59.0 cm., and $4\pi n = 551.6$.

M, the magnetometer is of the ordinary construction, namely four small magnets attached to the back of a small mirror, suspended by a spider's web-line.[1]

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1 It was afterwards found that this form of the magnetometer, though convenient, is not very accurate, for the curvature of the mirror changes according to the atmospheric conditions

C is the "compensating coil," which is wound on a small wooden reel, of diameter 4.75 cm. and breadth about 9 mm. This could slide along a groove in front of the magnetometer, perpendicular to the magnetic meridian. Its action on the magnetometer is opposite to that of the iron wire, so that it serves for compensating the so-called *immediate effect* of the magnetisation on the magnetometer.

T is the contact maker, consisting of a small dish half full of mercury and a metallic ball connected with a spring. As long as the ball is kept above the mercury surface, there is no circuit, but when it is allowed to descend, which it is always ready to do by means of the spring, contact is at once made.

K is the ordinary mercury switch for rapidly reversing the current.

G is an ordinary tangent galvanometer for measuring the current strength.

L is the liquid rheostat which serves to vary the E. M. F. of the main circuit gradually, so that the iron wire can be subjected to the process of demagnetisation by reversals. The zinc plates have the diameter of 5 cm. and are thoroughly amalgamated from time to time, when in use. The cylinder is nearly 45 cm. high.

R is a resistance box, and B is a battery of six gravity Daniell's cells. One end of the wire from the battery is joined to the resistance box and through this to one of the terminal plates of the liquid rheostat, while the other end is connected with the other terminal plate. The main circuit includes the magnetising solenoid, S, the compensating coil, C, and the galvanometer, G, and its ends are connected one with the lowest plate and the other with the middle plate of the liquid rheostat, the latter plate being moved up and down by means of a long string passing over a pulley. Of course, the magnetometer, the galvanometer, the liquid rheostat, the resistance box, and the battery are placed at sufficient distances from one another to be beyond mutual influence.

The magnetometer stands magnetically east of the iron wire, and receives light from a slit placed 1 metre off, the image of which it reflects upon a millimeter scale just above the slit. The arrangement is so made that when the image is just over the slit, the magnetometer is free from any deflecting force.

The distance of the magnetometer from the nearest pole of the iron wire is 5.9 cm. The intensity of magnetisation per 1 mm. of the scale is .119 C. G. S.

Method of Observation.

The wire to be tested was heated to redness in a porcelain tube and was well annealed. It was then carefully taken out of the tube and was hung inside the solenoid. By subjecting it to the process of demagnetisation by reversals, any trace of magnetisation could be taken away. The next process was to determine a proper position for the compensating coil, C, so as to cancel the *immediate effect* of the magnetisation of the wire on the magnetometer. A certain position being given to the coil, a current was instantaneously sent by the contact maker, T. If there were any sudden deflection of the image, the coil was moved towards or away from the magnetometer in such a way as to cancel as much as possible the initial sudden deflection. This process was repeated, if necessary, until a position was determined for the coil, such that, on passing the current, there was no apparent sudden deflection of the image, but a slow and continuous motion of it along the scale. Then the wire was once more demagnetised by reversals and the current was suddenly made. The position of the image, as it slowly crept along the scale, was read by eye-and-ear method at various instants after "make."

Of course, a new determination of the position of the coil was necessary for each new current.

In the following tables, which show some of my experiments, the time is given in seconds after "make," the magnetising forces are reduced to C.G.S., while the amount of creeping is given in mm. of the scale.

Exp. 1. No load. (Pl. VII.)										
Time. \ Field.	.0282	.0569	.0873	.127	.235	.461	.733	1.00	1.53	1.55
0	0	0	0	0	0	0	0	0	0	0
2	.55	1.0	2.2	2.7	4.5	10.7(?)	...	...	...	...
5	.7	1.5	3.0	4.1	7.0	13.7	22.6	43.8	139.6	148.1
10	.8	1.9	3.75	5.1	8.2	15.5	24.6	46.7	141.6	150.1
15	.85	...	3.9	5.3	9.0	15.9	25.6	47.8	143.1	151.6
20	.9	1.9	3.9	5.4	9.1	16.7	26.3	48.7	143.7	152.1
30	.9	2.0	4.0	5.8	9.5	16.8	27.1	49.4	145.6	153.6
40	.9	2.0	4.0	5.9	9.8	17.3	27.4	49.8	146.7	154.6
50	.9	2.0	4.15	6.0	9.9	17.6	28.0	...	147.3	155.1
60		2.0	4.2	6.0	10.0	17.7	28.1	50.7	147.6	156.2
80			4.3	6.1	10.1	17.8	28.2	50.9	148.5	156.6
100			4.3	6.1	10.2	17.9	28.4	51.3	149.1	157.1
120						18.2	28.9	51.5	149.5	157.4
150							29.0	51.7	149.7	158.1
180							29.1	51.8	150.5	158.3
Defln. compensated.	3.5	7.7	12.3	19.4	41.6	104	194	302	517	523

Exp. 2. Under 2 kilos.=.445 kilo. per sq. mm. (Pl. VIII.)

Time. \ Field.	.0273	.0538	.0868	.126	.232	.452	.733	.993	1.56
0	0	0	0	0	0	0	0	0	0
2	.2	1.1	1.9	3.0	5.4	12.0	...	...	...
5	.5	1.7	2.9	4.4	8.4	14.8	31.9	45	172
10	.8	2.0	3.5	5.2	9.5	16.3	33.7	47.0	174.0
15	.9	2.1	3.8	5.5	10 1	17.2	34.6	47.9	176.2
20	.9	2.2	3.9	5.6	10.4	17.7	35.2	48.5	177.4
30	1.0	2.2	3.9	5.7	10.6	18.1	35.9	49.4	178.3
40	1.0	2.3	4.0	5.8	10.7	18.3	36.3	50.0	179.1
50	1.0	2.3	4.0	6.0	11.0	18.7	36.7	50.2	180.0
60	1.0	2.3	4.0	6.2	11.1	18.8	36.8	50.6	180.2
80		2.4	4.0	6.2	11.2	19.0	37.0	50.9	181.0
100		2.4	4.1	6.3	11.3	19.1	37.5	51.1	181.2
120				6.3	11.4	19.1	37.7	51.4	182.0
150					11.4	19.3	37.8	51.7	182.3
180					11.5	19.5	37.9	52.0	183.0

Exp. 3. Under 5 kilos.=1.11 kilos. per sq. mm. (Pl. IX.)

Time. \ Field.	.273	.0538	.0873	.127	.232	.456	.731	.993	1.56
0	0	0	0	0	0	0	0	0	...
2	.6	1.0	2.0	2.6	6.6	13.3	...	...	...
5	.9	1.9	3.0	4.3	8.8	16.3	28.9	53.1	...
10	.9	2.0	3.3	4.8	10.3	18.3	30.8	55.2	...
15	.9	2.05	3.5	5.4	10.9	19.2	31.8	56.3	1.3
20	1.0	2.2	3.7	5.5	11.5	19.5	32.3	57.1	2.4
30	1.0	2.3	3.85	5.5	11.7	20.3	33.0	58.0	3.8
40	1.0	2.4	3.9	5.6	11.9	20.5	33.4	58 4	4.7
50	1.05	2.5	3.9	5.65	12.3	20.8	33.8	59.0	5.5
60	1.05	2.5	3.95	5.7	12.4	21.1	33.9	59.2	5.8
80	1.1	2.55	4.1	5.8	12.6	21.25	34.1	59.4	6.8
100		2.6	4.1	5.85	12.7	21.4	34.5	59.9	7.2
120		2.6	4.2	5.9	12.8	21.6	34.8	60.1	7.7
150				6.0	12.9	21.8	34.9	60.2	8.15
180				6.1	13.1	22.0	35.0	60.4	8.7
200									8.9

Exp. 4. Under 15 kilos. =3.34 kilos. per sq. mm. (Pl. X.)									
Field. / Time.	.0282	.0538	.0870	.127	.232	.456	.732	1.00	1.56
0	0	0	0	0	0	0	0	0	...
2	.5	1.3	2.6	4.3	7.5(?)	...	...	...	...
5	1.0	2.1	3.85	5.7	10.0	18.8	34.2	60.1	...
10	1.2	2.5	4.6	6.8	11.3	20.4	35.5	62.6	2.9
15	1.2	2.75	4.9	7.3	11.9	21.2	36.5	63.6	4.1
20	1.2	2.9	5.0	7.5	12.0	21.5	37.0	64.2	5.1
30	1.3	3.0	5.1	7.7	12.4	22.1	37.7	65.2	6.3
40	1.3	3.0	5.15	7.8	12.8	22.3	38.1	65.9	7.2
50	1.3	3.05	5.2	7.8	12.85	22.5	38.5	66.1	7.9
60	1.35	3.1	5.3	7.8	12.9	22.6	38.7	66.6	8.2
80		3.1	5.3	7.9	13.0	23.0	38.9	67.0	9.0
100			5.4	7.9	13.05	23.1	39.2	67.15	9.9
120			5.5	8.0	13.1	23.2	39.4	67.3	10.1
150			5.5	8.1	13.2	23.3	39.6	67.95	10.8
180				8.2	13.3	23.4	39.7	68.1	11.1
200								68.2	11.3

Discussion of the Preceding Experiments.

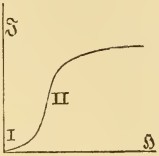
The figures representing the result of the above experiments show that when the field is very weak, everything goes on smoothly. But when the field strength gets somewhat greater, there appears to be an enormous growth of magnetisation during a very short time just after "make," and further this initial growth increases with the load. Two possible explanations may be given of this phenomenon.

(1°) It may be not the proper *growth*[1] in magnetisation, but

1 This term is substituted for *creeping*, because the process is not slow here

simply the result of some secondary time effect due to imperfections of our experimental method. To point out the possible defects, we must first of all have a clear grasp of the meaning of the term "compensation." When a current is sent through the solenoid, the iron wire will be magnetised and will act on the magnetometer, which will thus begin to be deflected with a certain acceleration. Now, the current circulating in the compensating coil exercises just the contrary action on the magnetometer. By trials, we strive to make these two contrary effects on the magnetometer as nearly equal as possible, which condition we can decide by looking at the image given by the mirror of the magnetometer on a scale placed at a distance of 1 metre. If the image does not move suddenly on pressing the key, we take it to be all right. This will be quite correct, if the magnetised iron and the compensating coil get their respective full strengths at once. But as we know, owing to the self-induction, which in the present case is not small, the current does not attain its final value at once, and though the time required for attaining this final state be very small, yet it will certainly be comparable with the interval, during which the mirror of the magnetometer is accelerated enough to produce such a small motion as our eyes can just perceive by its image at a distance of 1 metre. In other words, the current, and with it the intensity of magnetisation, will continue to increase after the instant at which we decide the state of compensation. Now, this fact, if it be present, will be of no importance so long as the intensity of magnetisation increases in a simple proportion with the strength of field, which in its turn increases in a simple proportion with the current. In this case then the whole subsequent deflection will be wholly due to the "growth in magnetisation." In fact, this is just the case with a very weak field, where $\frac{d\mathfrak{I}}{d\mathfrak{H}}$ is constant. But when the field begins to get somewhat great, the curve of magnetisation

begins to he turned, and $\frac{d^2\mathfrak{J}}{d\mathfrak{H}^2}$ has now a certain positive and finite value. Thus near the portion lying between the first and the second stage of the curve of magnetisation, the intensity of magnetisation increases in a greater ratio than that of a simple proportion. Therefore, if we denote the short interval which elapses before we can perceive the deflection of the image after "make," by τ, the compensation may be exact for $\frac{d\mathfrak{J}}{dt}\tau$, but not sufficient for $\frac{d\mathfrak{J}}{dt}t$, where t denotes a second, for instance. The result is that the compensation is soon found to be insufficient, and there follows the deflection of the magnetometer in the positive direction (*i. e.*, in that direction in which the magnetometer strives to drive it), which must be distinguished from that due to pure growth of magnetisation in a constant field.



(2°) We may suppose all these disturbing actions to be over before the magnetometer can manifest its motion to our eyes on the scale, and hence accept the growth observed as a pure time-effect.

It seems to me that in stronger fields in my experiments, the circumstances are just such as are described in (1°). But even in that case, some at least of the initial magnetisation must be pure growth. How much, however, we can not tell ; possibly the greater portion is of that nature. After all, what is called the *immediate effect* can have no definite limit. For, since it denotes the amount of the magnetisation compensated at the instant when the deflection of the magnetometer can just be perceived, it will depends largely on the constants of the particular magnetometer ; for instance, on its moment of inertia, the co-efficient of damping, the controlling force, etc., as well as on the co-efficient of self-induction of the particular solenoid. Speaking

rigorously there can be no such thing as absolutely immediate effect, and Ewing surely means by the *immediate effect* an effect which is produced immeasurably fast. But one will easily see that there can be no sharp demarcation separating the immeasurably rapid *immediate effect* from the extremely slow *creeping*, but that the change from one to the other will occur gradually and continuously.

Such being the case, in order to compare the rate of *growth* under various circumstances, we must have recourse to some other means than that of merely subtracting the *immediate effect*, as determined by *compensation*, from the subsequent readings.

I therefore endeavoured to find the curves giving the relation between the intensity of magnetisation at the several instants and the corresponding times, by means of an equation, and to compare the constants thereby obtained. For that purpose the series of more careful experiments which follow were made.

Experiment 5 gives the ordinary curve of magnetisation, the readings being reduced to those at 15 seconds after "make."

The other experiments give the time curve. The first column gives the time in seconds after "make." The second column gives the readings in mm. corresponding to the several instants in the first column. The third column gives similar readings taken once more immediately after subjecting the wire to the process of demagnetisation by reversals.

Exp. 5. (§ 5) curve under no load. (Pl. XI.)									
Field.	.0537	.0866	.125	.246	.443	.682	.949	1.59	1.80
Deflection.	9.2	16.0	24.0	54.2	115.5	199.0	323.6	720.2	901.0
Intensity.	1.10	1.91	2.94	6.41	13.8	23.7	38.6	85.9	107.5

All the readings are properly corrected, and reduced to those at 15 seconds after "make."

Exp. 6. No load. $\mathfrak{H}$ = 251 (Pl. XI.)			Exp. 7. 15 kilos. $\mathfrak{H}$ = .25 (Pl. XI.)		
Time.	Readings.		Time.	Readings.	
0	203.0	203.1	0	191.1	191.9
5	211.1	211.8	5	198.2	199.0
10	212.3	2.9	10	199.6	200.0
15	2.9	3.2	15	200.0	0.3
20	3.1	3.7	20	0.2	0.65
30	3.32	3.9	30	0.7	0.9
40	3.7	4.0	40	0.9	1.05
50	3.88	4.08	50	0.98	1.08
60	3.9	4.1	60	1.0	1.1
80	4.02	4.2	80	1.08	1.18
100	4.05	4.3	100	1.2	1.25
120	4.1	4.5	120	1.35	1.28
140	4.2	4.6	140	1.5	1.4
160	4.25	4.65	160	1.62	1.5
180	4.3	4.7	180	1.7	1.55
200	4.4	4.78	200	1.8	1.6
220	4.4	4.85	220	1.85	1.65
240	4.52	4 88	240	1.88	1.65
260	4.55	4.9	260	1.9	1.7
280	4.62	4.95	280	1.92	1.8
300	4.7	4.98	300	1.92	1.8
320	4.75	4.98	320	1.95	1.82
340	4.8	5.0	340	1.98	1.85
360	4.9	5.0	360	2.0	1.85
380	4.9	5.0	380	2.0	1.9
400	4.9	5.0	400	2.0	1.9
420	4.9		420	2.0	1.9
440	4.9		440	2.0	1.9
460	4.9		460	2.0	1.9
480	4.92		480	2.0	1.9

Exp. 8. No load. $\mathfrak{H}$=.254			Exp. 9. 15 kilos. $\mathfrak{H}$=.254		
Time.	Readings.		Time.	Readings	
5	9.9	0.4	5	2.0	3.2
10	11.52	1.8	10	3.3	4.28
15	2.1	2.5	15	3.98	4.82
20	2.4	2.7	20	4.32	5.0
30	2.8	3.18	30	4.9	5.28
40	3.0	3.4	40	5.02	5.38
50	3.08	3 5	50	5.1	5.5
60	3.12	3.58	60	5.3	5.62
70	3.2	3.6	70	5.4	5.7
80	3.25	3.6	80	5.68	5.8
90	3.4	3.7	90	5.8	5.88
100	3.55	3.72	100	5.82	5.9
120	3.72	3.9	120	5.95	5.95
140	3.75	3.98	140	5.98	5.98
160	3.80	4.0	160	6.08	6.0
180	3.90	4.08	180	6.10	6.1
200	3.92	4.2	200	6.12	6.1
220	3.98	4.3	220	6.12	6.1
240	4.0	4.38	240	6.15	6.15
260	4.0	4.4	260	6.18	6.18
280	4.02	4.4	280	6.20	6.2
300	4.05	4.4	300	6.20	6.2
320	4.08	4.4	320	6.20	6.2
340	4.1	4.4	340	6.22	6.2
360	4.1	4.4	360	6.22	6.2
380	4.	4.4	380	6.25	6.22
400	4.2	4.4	400	6.25	6.22
420	4.2	4.4	420	6.25	6.22
440	4.2	4.42			
460	4.25	4.42			
480	4.3	4.42			
500	4.4	4.45			

Exp. 10. 15 kilos. $\mathfrak{H}=1.74$			Exp. 11. No load. $\mathfrak{H}=1.74$		
Time.	Readings.		Time.	Readings.	
10	5.5	5.7	10	2.3	2.7
15	7.0	7.0	15	4.02	4.3
20	7.9	7.98	20	5.02	5.42
30	9.12	9.18	30	6.62	6.9
40	10.0	10.1	40	7.62	7.8
50	0.88	0.8	50	8.22	8.7
60	1.3	1.2	60	8.9	9.0
70	1.88	1.78	70	9.2	9.6
80	2.1	2.1	80	9.8	9.82
90	2.5	2.2	90	10.0	10.1
100	2.8	2.48	100	10.1	10.5
120	3.1	3.1	120	10.7	10.82
140	3.62	3.42	140	11.0	11.2
160	4.0	3.85	160	11.3	11.58
180	4.2	4.08	180	11.6	11.8
200	4.6	4.2	200	11.9	11.9
220	4.8	4.3	220	12.0	12.0
240	4.95	4.7	240	12.08	
260	4.98	4.88	260	12.2	
280	5.0	5.0	280	12.3	
300	5.02	5.1	300	12.5	
320	5.1	5.15	320	12.68	
340	5.18	5.2	340	12.8	
360	5 3	5.28	360	12.9	
380	5.42	5.4	380	12.9	
400	5.62	5.5	400	12.92	
420	5.7	5.7	420	12,98	
440	5.8	5.72	440	13.0	
460	5.85	5.8	460	13.08	
480	5.92	5.9	480	13.1	
500	5.92	5.92	500	13.1	
540	5.98	5.98	540	13.2	
580	6.0	6.1	580	13.38	
600	6.02	6.12	600	13.48	
660	6.1	6.2	660	13.7	
720	6.2		720	13.88	

Exp. 12. No load. $\mathfrak{H}=.248$			Exp. 13. 20 kilos. $\mathfrak{H}=.247$		
Time.	Readings.		Time.	Readings.	
0	0		0	0	
2	...	6.9	2	...	8. ?
5	7.6	8.7	5	9.9	10.3
10	9.1	10.05	10	10.98	11.28
15	9.7	10.82	15	11.3	11.9
20	10.3	10.98	20	11.7	12.1
30	10.6	11.5	30	12.02	12.28
40	11.15	11.8	40	12.1	12.5
50	11.38	11.9	50	12.2	12.7
60	11.43	12.0	60	12.3	12.9
70	11.53	12.1	70	12.4	12.95
80	11.6	12.2	80	12.58	13.0
90	11.9	12.35	90	12.62	13.02
100	12.02	12.42	100	12.72	13.05
120	12.3	12.65	120	12.95	13.09
140	12.38	12.8	140	12.98	13.1
160	12.4	12.82	160	13.1	13.11
180	12.5	12.87	180	13.11	13.12
200	12.6	12.89	200	13.12	13.12
220	12.7	12.9	220	13.15	
240	12.88	12.92	240	13.17	
260	12.95	12.94	260	13.19	
280	13.05	12.96	280	13.21	
300	13.2	12.98	300	13.25	
320	13.25	13.0	320	13.3	
340	13.3	13.05	340	13.35	
360	13.3	13.15	360	13.4	
380	13.37	13.23	380	13.44	
400	13.39	13.26	400	13.46	
420	13.4	13.3	420	13.47	
440	13.41	13.3	440	13.48	
460	13.42		460	12.48	
480	13.42				
500	13.42				

Exp. 14. 20 kilos. $\mathfrak{H}=1.62$ (Pl. XII.)			Exp. 15. No load. $\mathfrak{H}=1.62$ (Pl. XII.)		
Time.	Readings.		Time.	Readings.	
10	0.98	1.3	10	2.3	3.4
15	2.4	2.6	15	4.0	4.9
20	3.2	3.52	20	5.04	5.92
30	4.9	5.1	30	6.5	7.1
40	5.88	6.1	40	7.5	8.0
50	6.48	6.5	50	8.05	8.9
60	7.1	7.28	60	8.9	9.1
70	7.75	7.62	70	9.15	9.8
80	8.02	8.2	80	9.75	10.0
90	8.5	8.32	90	10.0	.15
100	8.98	8.6	100	10.1	.5
120	9.4	9.38	120	10.8	1.0
140	9.98	9.6	140	11.02	1.1
160	10.12	10.2	160	11.5	1.6
180	10.5	10.28	180	11.8	
200	10.98	10.7	200	12.0	
220	11.05	11.1	220	12.1	
240	11.2	11.18	240	12.3	
260	11.5	11.32	260	...	
280	11.8	11.55	280	12.78	
300	11.95	11.75	300	12.98	
320	12 0	12.0	320	13.0	
340	12.02		340	13.0	
360	12.1		360	13.08	
380	12.22		380	13.12	
400	12.5		400	13.3	
420	12.6		420	...	
440	12.75		440	13.5	
460	12.9		460	13.62	
480	12.92		480	13.78	
500	12.98		500	13 82	
520	13.0		520	13.89	
540	13.02		540	13.90	
560	13.08		560	13.92	
580	13.1		580	13.95	
600	13.2		600	14.0	

Calculations.

The equation which I have assumed for the relation between the intensity of magnetisation and time under a constant field is

$$\mathfrak{J} = a - \cdots\cdots\cdots - le^{-\lambda t} - me^{-\mu t} - ne^{-\nu t} - pe^{-\pi t},$$

where $\lambda > \mu > \nu > \cdots\cdots\cdots\cdots\cdots$

Now, on drawing the figures exactly as they were given by the observations, I found that the curves had some irregularities, so that the values could not be made use of directly in the calculations of the several constants. I drew, therefore, a smoothed curve, which may be called the mean curve, lying as closely as possible to the actual curve in each case, and from the values obtained from this mean curve, calculations were made. As the process is rather laborious, I took only six of the above experiments. In Exp. 7 and 8, the mean of two successive observations is taken in drawing the curves, but for all the rest the first observation alone is used.

Ex. 8. No load. $\mathfrak{H}=.254$ (Pl. XIII.)

Time.	Mean readings.	Mean curve.	Calc.
5	0.00	0.00	0.00
10	1.51	1.52	1.53
15	2.15	2.11	2.11
20	2.40	2.40	2.40
30	2.81	2.74	2.74
40	3.05	2.95	2.95
50	3.14	3.10	3.10
60	3.20	3.21	3.21
70	3.25	3.31	3.31
80	3.28	3.39	3.39
90	3.40	3.46	3.46
100	3.49	3.52	3.52
120	3.66	3.64	
140	3.72	3.73	<3.75
160	3.75	3.80	
180	3.84	3.86	
200	3.91	3.908	3.908
220	3.99	3.951	
240	4.04	3.992	
260	4.05	4.027	
280	4.06	4.055	
300	4.08	4.076	4.079
320	4.09	4.096	
340	4.10	4.113	
360	4.10	4.130	
380	4.15	4.145	
400	4.15	4 158	4.154
420	4.15	4.170	
440	4.16	4.181	
460	4 19	4.191	
480	4.21	4.200	
500	4.28	4.209	

$a=4.213$, l, λ unknown

$m=6.14$ $n=1.568$ $p=1.572$

$\mu=.276$ $\nu=.062$ $\pi=.0082$

$\frac{\mu}{\nu}=4.45$ $\frac{\nu}{\pi}=7.57$

Exp. 9. 15 kilos. $\mathfrak{H}=.254$ (Pl. XIII.)

Time.	Mean readings.	Mean curve.	Calc.
5	2.5	2.50	2·50
10	3.69	3.70	3.70
15	4.30	4.20	4.20
20	4.56	4.52	4.52
30	4.99	4.93	4.93
40	5.10	5.167	5.17
50	5.20	5.332	5.33
60	5.36	5.460	5 45
70	5.45	5.549	5.55
80	5.64	5.627	5.63
90	5.74	5.690	5.69
100	5.76	5.741	5.74
120	5.85	5.826	
140	5.88	5.889	<5.91
160	5.94	5.940	
180	6 00	5.981	
200	6.01	6.011	6.006
220	6.01	6.036	
240	6.05	6.056	
260	6.08	6.073	
280	6.10	6.087	
300	6.10	6.099	6.098
320	6.10	6.109	
340	6.11	6.118	
360	6.11	6.125	
380	6.14	6.132	
400	6.14	6.138	6.139
420	6.14		

$a=6.174$

$l=5.78$ $m=2.084$ $n=1.16$ $p=.74$

$\lambda=.4416$ $\mu=.093$ $\nu=.026$ $\pi=.0076$

$\frac{\lambda}{\mu}=4.75$ $\frac{\mu}{\nu}=3.58$ $\frac{\nu}{\pi}=3.42$

Exp. 12. No load. $\delta = .248$ (Pl. XIV.)

Time.	Readings.	Mean curve.	Calc.
5	7.6	7.60	7.59
10	9.1	9.11	9.12
15	9.7	9.80	9.80
20	10.3	10.22	10.19
30	10.6	10.68	10.67
40	11.15	11.01	11.01
50	11.38	11.25	11.25
60	11.43	11.45	11.45
70	11.53	11.61	11.62
80	11.6	11.75	11.76
90	11.9	11.89	11.89
100	12.02	12.00	11.99
120	12.3	12.19	12.19
140	12.38	12.35	<12.43
160	12.4	12.49	
180	12.5	12.62	
200	12.6	12.73	12.73
220	12.7	12.828	
240	12.88	12.913	
260	12.95	12.986	
280	13.05	13.054	
300	13.2	13.114	13.115
320	13.25	13.168	
340	13.3	13.216	
360	13.3	13.257	
380	13.37	13.293	
400	13.39	13.326	13.321
420	13.4	13.355	
440	13.41	13.379	
460	13 42	13 400	
480	13.42	13.417	
500	13.42	13.430	13.432

$a = 13.559$ λ, l unknown

$m = 5.23$ $n = 1.99$ $p = 2.89$

$m = .237$ $\nu = .047$ $\pi = .00625$

$\frac{\mu}{\nu} = 5.04$ $\frac{\nu}{\pi} = 7.5$

Exp. 13. 20 kilos. $\delta = .247$ (Pl. XIV.)

Time	Readings.	Mean curve.	Calc.
2	7.5?	7.5?	7.87
5	9.9	9.9	9.90
10	10.98	10.97	10.93
15	11.3	11.355	11.35
20	11.7	11.62	11.62
30	12.02	11.95	11.95
40	12.1	12.14	12.16
50	12.2	12.29	12.30
60	12.3	12.42	12.42
70	12.4	12.51	12.51
80	12.58	12.59	12.59
90	12.62	12.66	12.66
100	12.72	12.72	12.72
120	12.95	12.83	
140	12.98	12.92	<12.95
160	13.10	13.00	
180	13.11	13.06	
200	13.12	13.11	13.10
220	13.15	13.16	
240	13.17	13.202	
260	13.19	13.24	
280	13.21	13.27	
300	13.25	13.30	13.30
320	13.30	13.33	
340	13.35	13.36	
360	13.4	13.38	
380	13.44	13.40	
400	13.46	13.42	13.42
420	13.47	13.44	
440	13.48	13.456	
460	13.48	13.47	
480			
500			13.50

$a = 13.621$

$l = 5.28$ $m = 1.804$ $n = .855$ $p = 1.299$

$\lambda = .45$ $\mu = .093$ $\nu = .023$ $\pi = .00466$

$\frac{\lambda}{\nu} = 4.84$ $\frac{\mu}{\nu} = 4.04$ $\frac{\nu}{\pi} = 4.93$

Exp. 11. No load. $\mathfrak{H}=1.74$ (Pl. XV.)

Time.	readings.	Mean curve.	Calc.
10	2.3	2.30	2.30
15	4.02	3.95	3.95
20	5.02	5.14	5.14
30	6.62	6.69	6.69
40	7.62	7.66	7.66
50	8.22	8.35	8.34
60	8.9	8.88	8.85
70	9.2	9.29	9.27
80	9.8	9.64	9.63
90	10.0	9.94	9.94
100	10.1	10.20	10.20
120	10.7	10.65	
140	11.0	11.01	<11.15
160	11.3	11.30	
180	11.6	11.54	
200	11.9	11.74	11.75
220	12.0	11.93	
240	12.08	12.10	
260	12.20	12.25	
280	12.3	12.38	
300	12.5	12.50	12 49
320	12.68	17.61	
340	12.8	12.71	12.70
360	12.9	12.80	
380	12.9	12.88	
400	12.92	12.96	12.96
420	12.98	13.03	
440	13.0	13.10	
460	13.08	13.16	
480	13.10	13.22	
500	13.1	13.27	13.27
540	13.2	13.368	
580	13.38	13.458	
600	13.48	13.500	13.48
660	13.7		
720	13.88		

$a=13.946$, l, λ unknown

$m=8.145$ $n=4.792$ $p=4.452$

$\mu=.087$ $\nu=.0194$ $\pi=.00377$

$\frac{\mu}{\nu}=4.49$ $\frac{\nu}{\pi}=5.14$

Exp. 10. 15 kilos. $\mathfrak{H}=1.74$ (Pl. XV.)

Time.	Readings.	Mean curve.	Calc.
10	5.6	5.6	5.6
15	7.0	7.0	6.98
20	7.94	7.94	7.93
30	9.15	9.24	9.24
40	10.05	10.11	10.11
50	10.84	10.75	10.75
60	11.25	11.26	11.26
70	11 83	11.70	11.69
80	12.10	12.05	12 05
90	12.35	12.36	12.365
100	12.64	12.64	12.64
120	13.10	13.11	
140	13.52	13.48	<13.66
160	13.93	13.80	
180	14.14	14.06	
200	14.14	14.31	14.31
220	14.55	14.52	
240	14.83	14.70	
260	14.93	14.85	
280	15.00	14.99	
300	15.06	15.105	15.093
320	15.13	15.209	
340	15.19	15.310	
360	15.29	15.405	
380	15.41	15.489	
400	15.56	15.564	15.562
420	15.70	15.635	
440	15.76	15.700	
460	15.83	15.760	
480	15.91	15.813	
500	15.92	15.865	15.865
540	15.98	15.955	
580	16.05	16.030	
600	16.07	16.065	16.065
620			

$a=16.458$

$l=8.34$ $m=5.50$ $n=4.59$ $p=4.60$

$\lambda=.38$ $\mu=.081$ $\nu=.018$ $\pi=.0041$

$\frac{\lambda}{\mu}=4.69$ $\frac{\mu}{\nu}=4.5$ $\frac{\nu}{\pi}=4.39$

Concluding Remarks.

Since the nature of magnetism is not well known, I cannot give any rigorous reasoning leading to the above equation. But meanwhile let us try to explain it by the molecular theory. According to this theory, the molecules of iron which find themselves on the outer surface of the wire, are less constrained by the mutual action of the molecules than those situated in the interior, and hence are more ready to submit to the action of any disturbing cause. Therefore, if a given magnetic force is applied to the wire these surface molecules are first affected. Then the molecules lying next the outermost have their stability reduced, and will be the next to submit, and so on. Thus, the process of magnetisation diffuses itself gradually from the outermost layer into the interior of the mass. Hence, from analogy with Fourier's solution of the propagation of heat, we may put, in a cylindrical conductor,

$$\mathfrak{I} = a - \sum_{n=o}^{\infty} c_n e^{-k_n t}.$$

Now, since we cannot of course use an infinite number of terms in the actual calculation, we must cut down the expression and reduce it to a small finite number of terms. But this cutting out terms can not be done without somewhat affecting the values of c and k in some at least of the surviving terms. For, although as regards those terms which we are going to neglect, the values of the c's are small, yet the values of the k's are also small, and the terms cannot, therefore, be neglected in the ordinary way. But, as long as t is not large, we can *approximately* substitute the sum of all these terms by a single term. For, let these terms be—

$$T = c_4 e^{-k_4 t} + c_5 e^{-k_5 t} + c_6 e^{-k_6 t} + \ldots\ldots\ldots\ldots\ldots\ldots$$

Since k is small and t is supposed to be not very large, kt may be taken as a small quantity. Hence, expanding, we have

$$T = e_1(1-k_1t)+c_2(1-k_2t)+c_3(1-k_3t)+\ldots\ldots\ldots\ldots\ldots\ldots$$
$$= c_1+c_2+c_3+\ldots\ldots\ldots \qquad -(c_1k_1+c_2k_2+c_3k_3+\ldots\ldots\ldots)t.$$

Hence we may put

$$T = Ce^{-Kt},$$

where

$$\left.\begin{aligned} C &= c_1+c_2+c_3+\ldots\ldots\ldots\ldots\ldots \\ K &= \frac{c_1k_1+c_2k_2+c_3k_3+\ldots\ldots\ldots}{c_1+c_2+c_3+\ldots\ldots\ldots} \end{aligned}\right\}$$

Thus, C is equal to the sum of all the c's, and K is the mean (in a certain sense) of all the k's of the terms to be replaced.

In my actual formula, p stands for C and π for K, and the fact that the p's are generally greater and the π's generally less than they ought to be, is in accordance with their nature, above explained.

Again, if we take one or two of the terms preceding $le^{-\lambda t}$, this formula can even express the whole curve in which the entire process of magnetisation is considered as a time effect, the magnetisation at t=o being zero. The growth in magnetisation immediately after the field is created will then be enormous. J. Hopkinson's experiments on a bundle of steel wires are particularly interesting in this connection, inasmuch as he showed that the curve for the frequency 72 per second was different from that for the frequency 5 per second, while the latter was almost identical with the statical one.[1]

Next, on examining the curves actually drawn from the observations (Pl. XI., XII.) we find some irregularities, which though they are of the order of a tenth of 1 mm. on the scale, must not, I think, be

1 *Loc. cit.* p. 358.

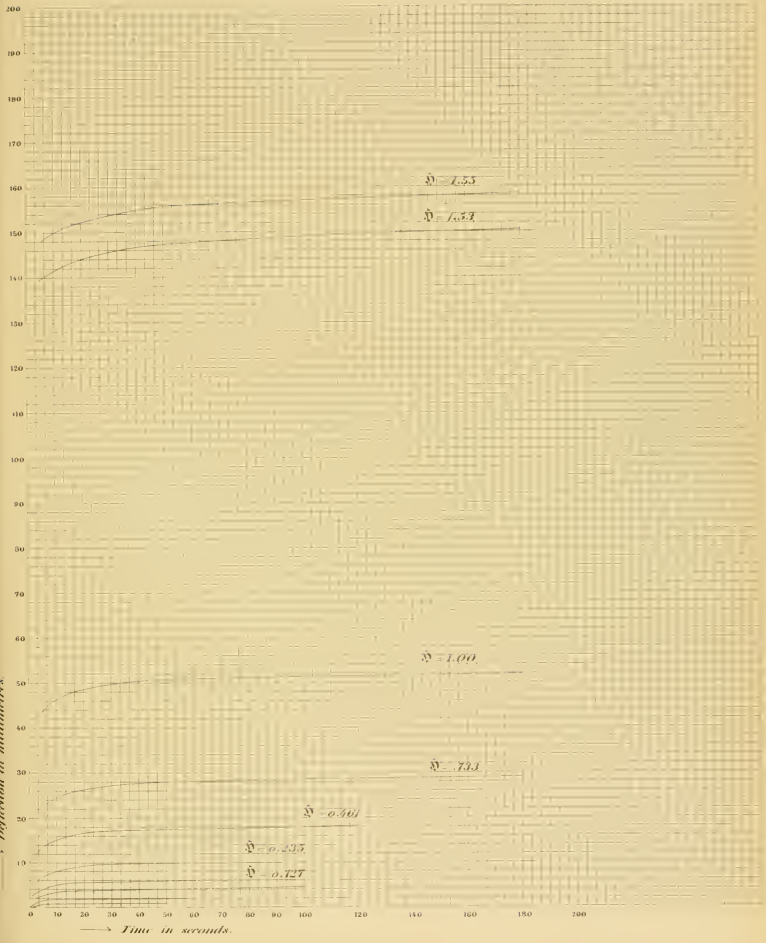
altogether looked upon as experimental errors, because they occur so regularly in relation to time. If forced to give an explanation of it, I would say that it is due to heterogeneity in the distribution of the molecules in the iron mass, some groups of molecules being more stable than others. Heterogeneity would seem to give hindrance to the diffusion of magnetisation. Thus, when the iron is well annealed, homogeneity will be obtained, and in this case magnetisation can diffuse more easily, which accounts for its great susceptibility in low fields and great rate of growth. On the other hand, when the homogeneity is broken by stretching the iron beyond its limit of elasticity, the susceptibility and the rate of growth are both reduced. In the latter case, and probably also in steel, the magnetisation will be only superficial. Grotrian is of opinion that an iron cylinder not very short in comparison with its diameter, exposed in a moderate magnetic field in its axial direction, is magnetised very unequally, the magnetisation being stronger at the circumference than in the interior.[1] Du Bois objects to this view, as being quite contrary to usual ideas, and explains the experimental results of Grotrian as being the effect of the demagnetising force.[2] The influence of the demagnetising force would, of course, lead to the same result, but from the later experiments[3] of Grotrian, it can be seen that this is not *the* only cause, and that the distribution of magnetisation is really that stated by Grotrian. This view has a certain likeness to the above explanation of the time-lag. But, after all, there is no certain ground, theoretical or experimental, for presenting the above explanation as representing the true nature of the process of magnetisation. I mean only this : that in the absence of any definite theory about the pheno-

1 *Wied. Ann.*, **50**, p. 703. (1893).
2 *Wied. Ann.*, **51**, p. 529. (1894).
3 *Wied. Ann.*, **52**, p. 733. (1894).

menon of time-lag, the above may be taken provisionally as accounting for something. I am quite ready to give it up when any theoretical advance supersedes its purpose.

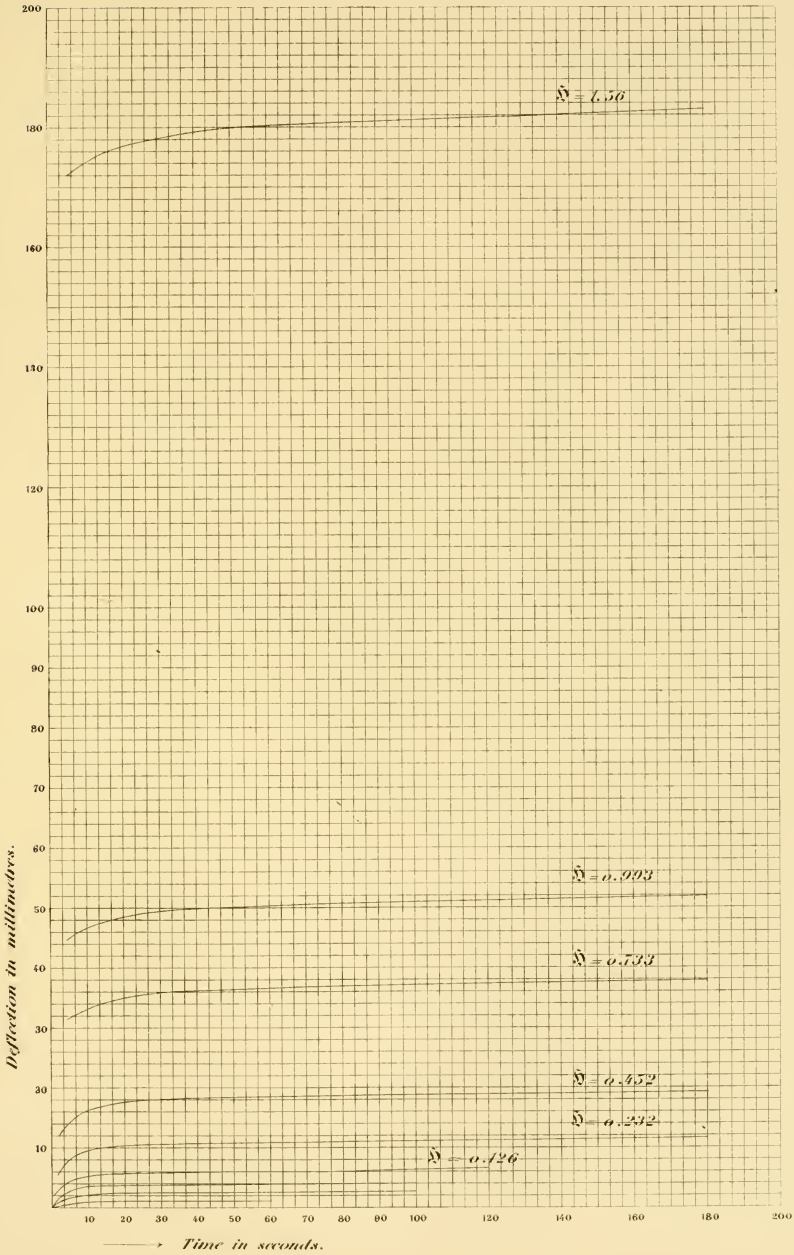
Before closing this paper, I must refer to that of Holborn, on the same subject, to which I had access while writing this. He used the method of Helmboltz's "Pendelunterbrecher," and the ballistic galvanometer. In one of his experiments, the specimen was a bundle of fine iron wires, each ·20 mm. thick. With a magnetising field of 48 C.G.S., the magnetising current reached its full strength after .00508 second, and with it the magnetisation also. With a magnetising field of 2 C.G.S., the magnetisation remained constant after .005 second. With a thicker wire, of diameter 4.5 mm., under a magnetising field of 50 C.G.S., the magnetising current reached its full strength after .01 second, and with it the magnetisation also. He concludes that as soon as the magnetising current reaches its full strength the magnetisation does so also; that is to say, there is no time effect in the magnetisation. I think that this conclusion can only be true within a certain degree of approximation. It is clear that in such a comparatively strong field as 50 C.G.S., the time-lag will be very small, especially in thin wires. But the case is different when the field is low and the wire is thicker. I should like very much to know whether he tried with the wire 4.5 mm. thick in a magnetising field of 2 C.G.S. and, if he did, what result he got.

1 *Sitzungsberichte, k. p. A. W.* (Berlin), *XI*, p. 173, 27, Feb. 1896.



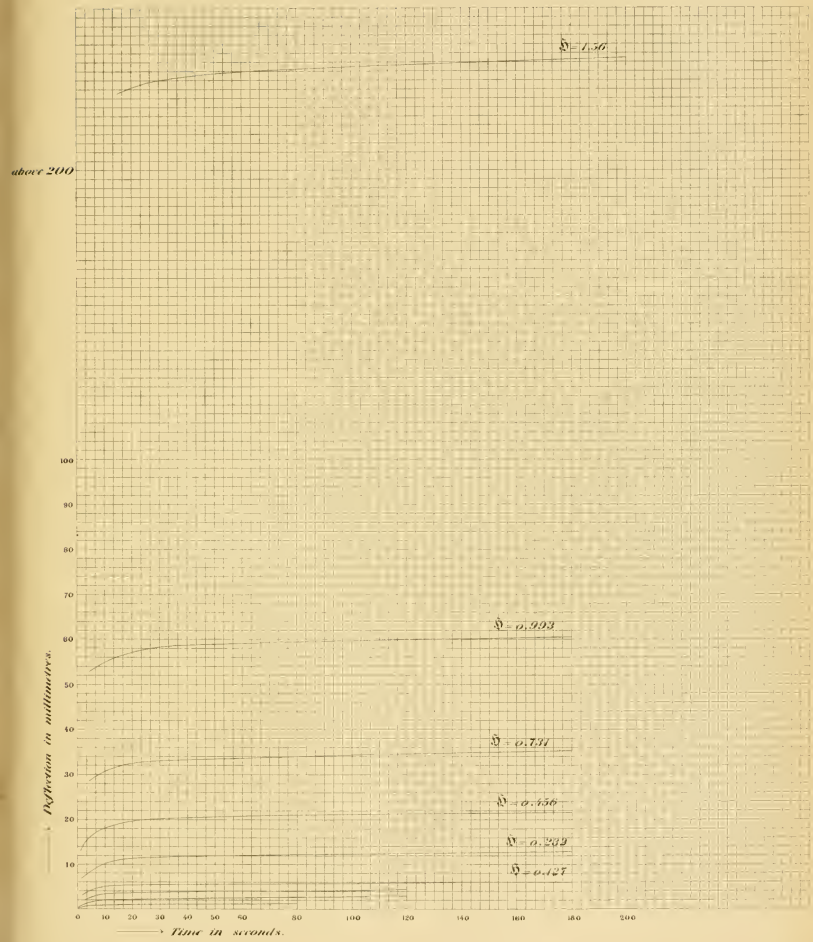
Θ for 1 mm. = 0.119

Load 2 kilos. = .45 kilo per square millimetre.



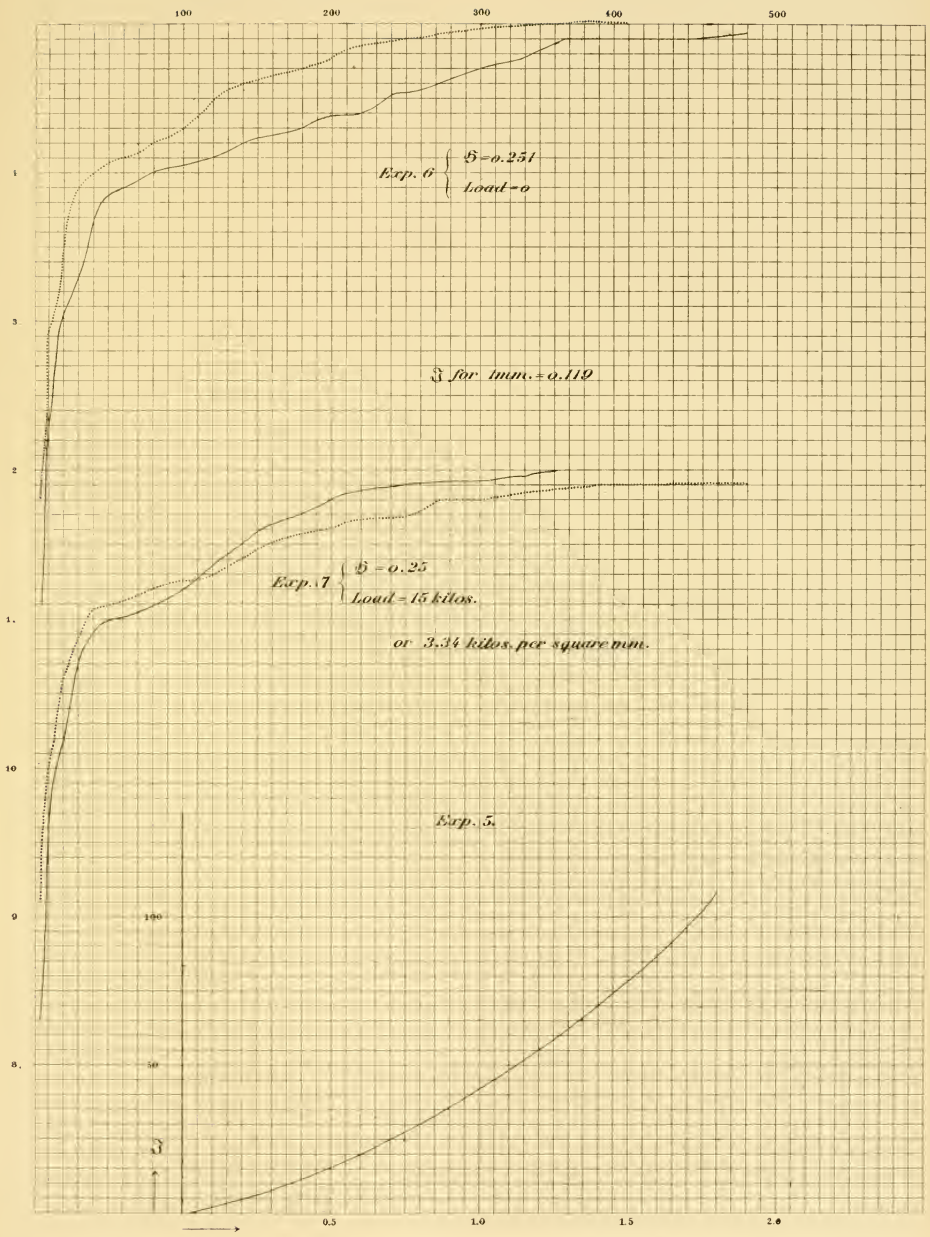
Ŷ for 1 mm = 0.119

Load 5 kilos. 4.41 kilos per square millimetre.

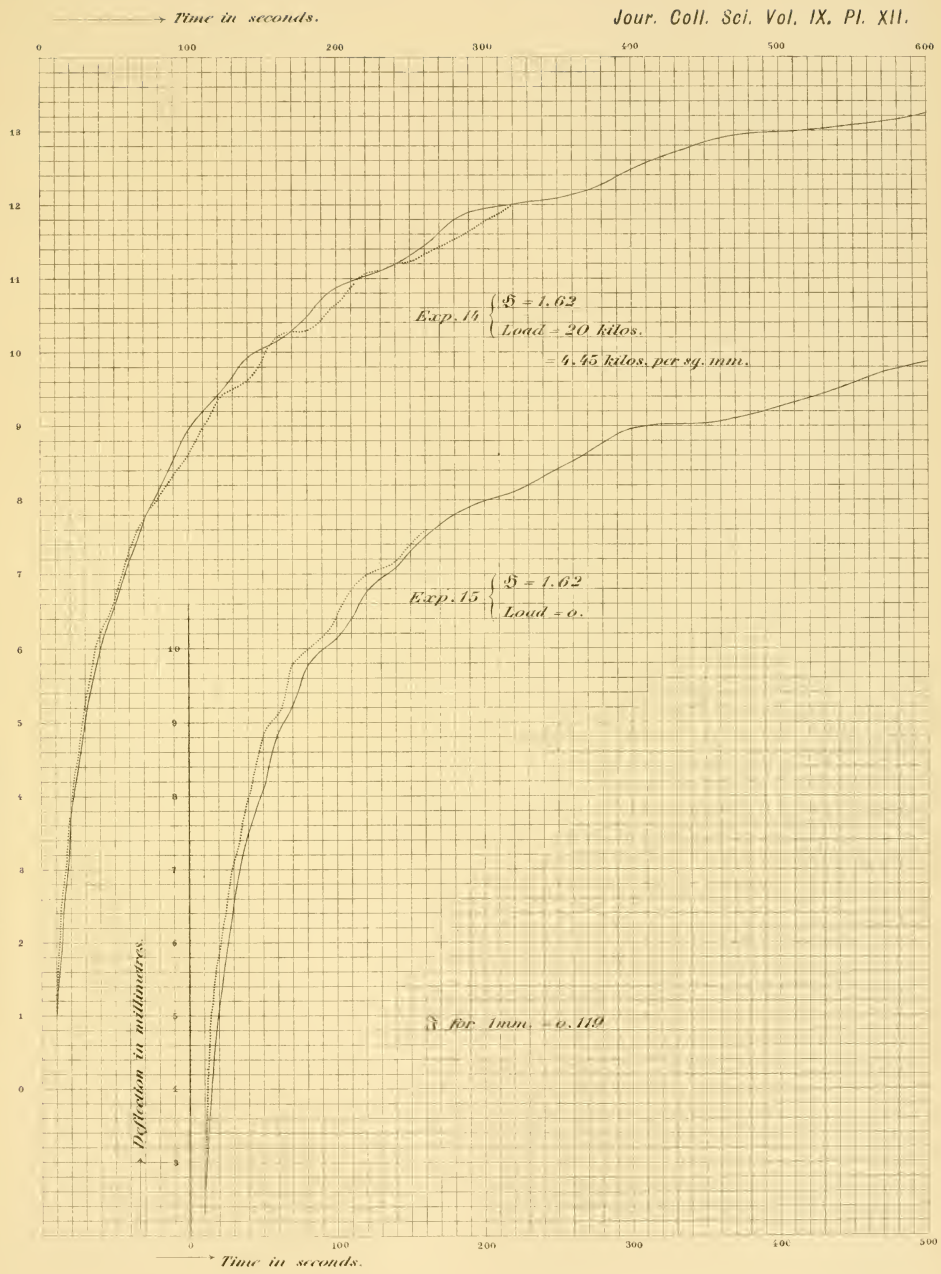


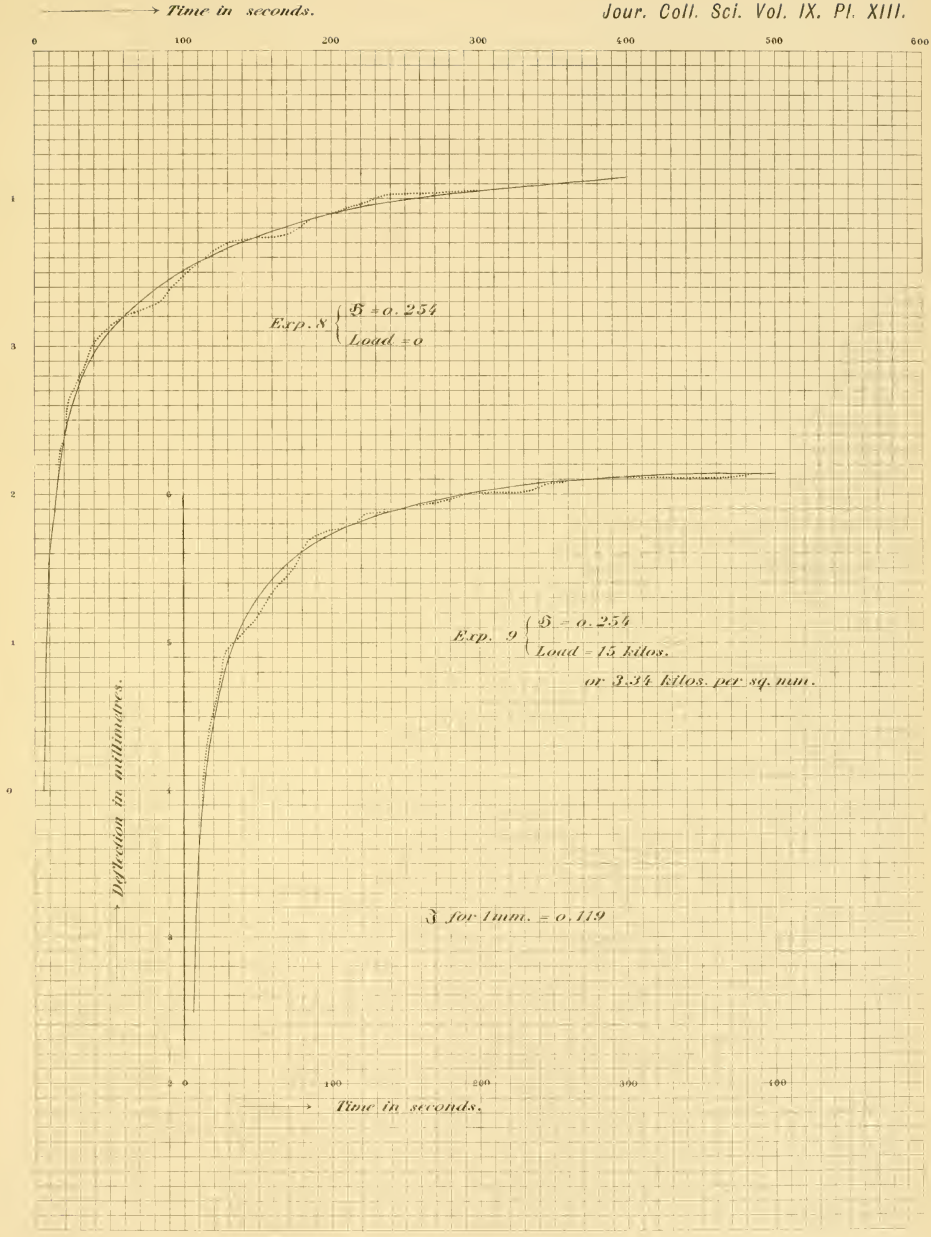
ϑ for 1 mm. = 0.119

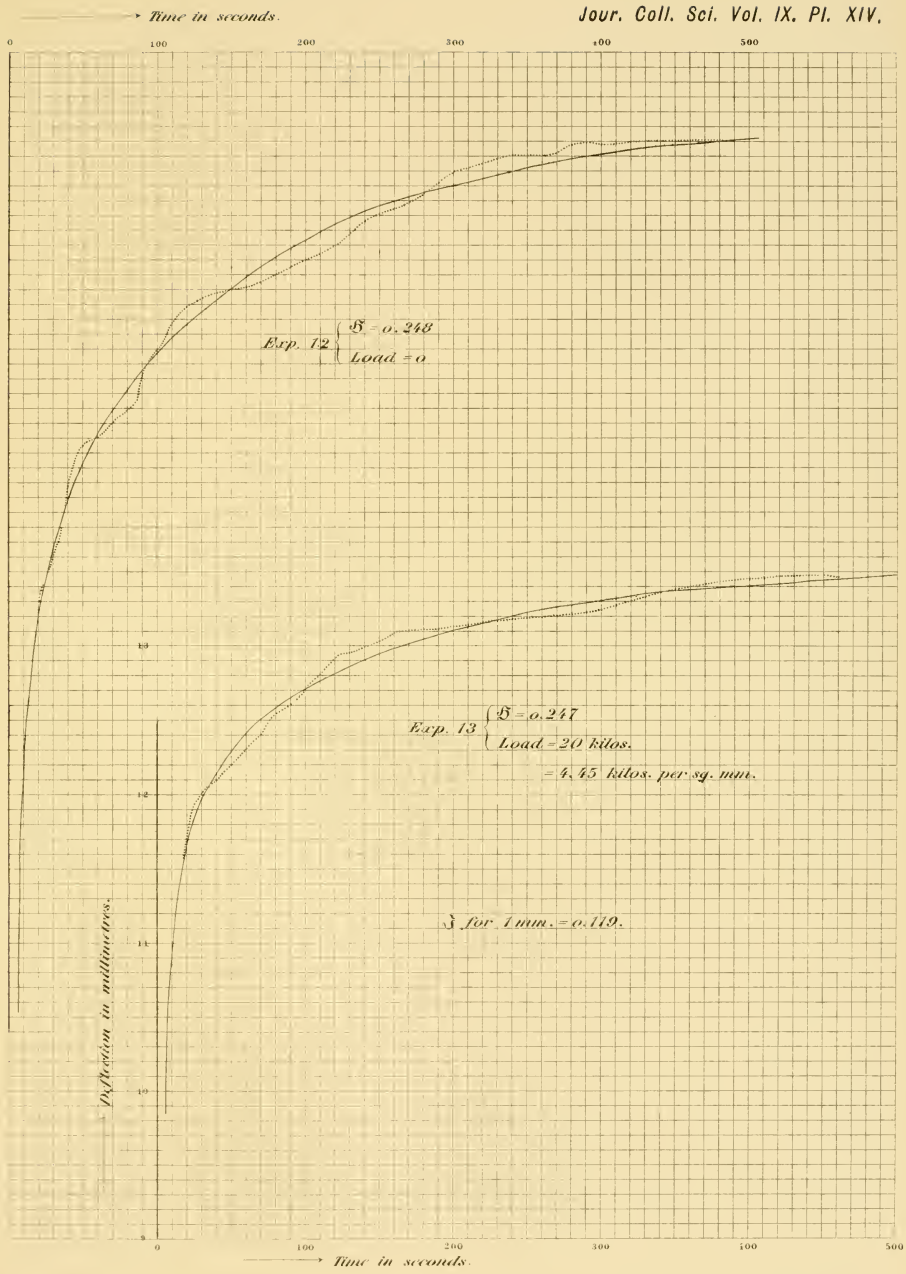
Ŝ for 1 mm = 0.119

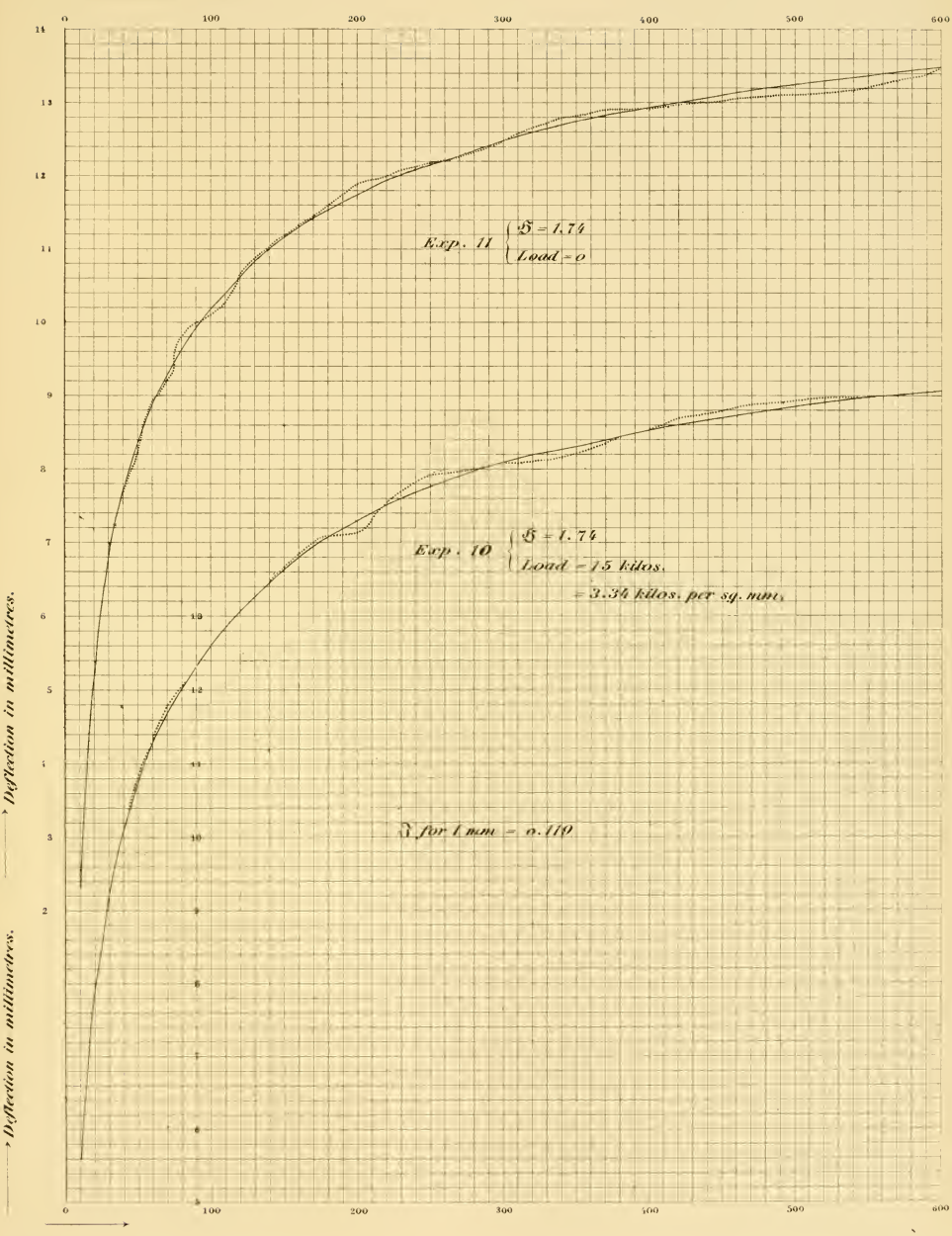


Curve of Magnetisation at 15 seconds after "Make."


Time in seconds.
0
100
200
300
400
500
600
Deflection in millimetres.
Exp. 14 { $\mathfrak{H}$ = 1.62
Load = 20 kilos.
= 4.45 kilos. per sq. mm.
Exp. 15 { $\mathfrak{H}$ = 1.62
Load = 0.
$\mathfrak{J}$ for 1mm. = 0.119
Deflection in millimetres.
Time in seconds.


Time in seconds.
0
100
200
300
400
500
600
Deflection in millimetres.
1
3
2
1
0
Exp. 8 { B = 0.254
Load = 0
Exp. 9 { B = 0.254
Load = 15 kilos.
or 3.34 kilos. per sq. mm.
Deflection in millimetres.
6
5
4
3
2
0
100
200
300
400
Time in seconds.


Time in seconds.
0
100
200
300
400
500
13
12
11
10
9
8
7
Deflection in millimetres.
Exp. 12 { $\mathfrak{H}$ = 0.248
Load = 0
Exp. 13 { $\mathfrak{H}$ = 0.247
Load = 20 kilos.
= 4.45 kilos. per sq. mm.
$\mathfrak{J}$ for 1 mm. = 0.119.
Deflection in millimetres.
Time in seconds.


Time in seconds.
Deflection in millimetres.
Deflection in millimetres.
Exp. 11
Load = 0
Exp. 10
Load = 15 kilos.
= 3.34 kilos. per sq. mm.
for 1 mm = 0.119

ERRATA.

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Page	Line				
88	3*	for	" says are "	read	" says, are."
104	2*	,,	" Maumené "	,,	" Fremy "
163	8	,,	" anp "	,,	" and "
164	7*	,,	" onə "	,,	" one "
174	3*	,,	" month "	,,	" mouth "
194	6	,,	" sulphate "	,,	" sulphide "
209	12	,,	" experiments. "	,,	" experiments)."
223	10	,,	" amidosulphonatel "	,,	" amidosulphonate,"
,,	15	,,	" methy,"	,,	" methyl "
232	9	,,	" neutra "	,,	" neutral "
244	10	,,	" che ical "	,,	" chemical "
245	bottom	,,	" dat epoint "	,,	" data point "
247	7*	,,	" imidosulphonate "	,,	" amidosulphonate "
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270 bottom, before 2nd			" = "	insert	", ∴ const."
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,,	3	,,	" 19 "	,,	" 103 "

* From bottom

Diffraction Phenomena in the Focal Plane of a Telescope with Circular Aperture due to a Finite Source of Light.

By

H. Nagaoka, *Rigakuhakushi,*

Professor of Applied Mathematics, Imperial University, Tōkyō.

With Plate XVI–XVII.

The diffraction phenomena due to a circular aperture have for a long time attracted the attention of physicists, on account of their intimate connection with the theory of optical instruments. For a point source of light, the problem has been treated by Airy,[1] and by Schwerd,[2] and again by Lommel[3], who has brought our knowledge of it to the highest state of perfection as regards both Fraunhofer's and Fresnel's diffraction phenomena. For practical purposes, it is necessary to modify the problem slightly, and investigate the diffraction due to a finite source of light, and this has been done, in connection with the resolving power or for the explanation of drop formation during the transit of inferior planets, by Rayleigh,[4] André,[5] Struve,[6] and Strehl.[7] In spite of these investigations, the field of research in this direction is far from being exhausted ; even the

1) Airy, *Camb. Phil. Trans.* **5**, 283. 1834.
2) Schwerd, *Beugungserscheinungen*, Mannheim, 1836.
3) Lommel, *Abhandl. d. bayer Akad.*, **15**, 1884.
4) Rayleigh, *Wave Theory of Light, Encycl. Brit.* 9th edition.
5) André, *Annales de l'École Normale*, (2) **5**, 275. 1876.
6) Struve, *Mémoires de l'Académie des Sciences de St. Petersbourg.* **30**. 1882.
Wied. Ann., **17**. 1008. 1882.
7) Strehl, *Zeitschrift für Instrumentenkunde*, **15**. 362. 1895.
„ „ „ **16**. 257. 1896.
„ „ „ **17**. 165. 1897.

simplest case involves complicated mathematical analysis, so that the result arrived at is only an approximation barely sufficient for practical purposes.

In the present paper, I give, in the first place, a general discussion of the Fraunhofer's diffraction phenomena of a circular aperture for a finite source of light. I then pass on to the consideration of the intensity of illumination both inside and outside a circular image, and show how, by the superposition of two systems of lines of equal intensity, we can explain the formation of a ligament during the ingress or egress of a dark disc over a luminous edge, as verified by the experiments of André and Angot.*

§ 1. General Expression for the Intensity.

It is well-known that the circular aperture of a telescope gives rise to a diffraction pattern, consisting of concentric rings with luminous centre, when the source of light is a point. If instead of a luminous point, we have a finite source of light, each of its elements will produce similar phenomena; so that the illumination in the focal plane of the telescope becomes the integral effect of all the points of light within a given geometrical area. Even with a uniform source, the intensity of the image is not uniform but, as is seen in the focal plane of the telescope, is distributed according to a law depending on the shape of the source and the size of the aperture.

Let the circular opening of the telescope be taken for the xy plane; denote the cosines of the angles which the incident ray makes with the x and y axes by α and β, and those for the diffracted ray by α' and β'. Putting R=radius of the telescope aperture, λ=wave length of light, $r=\frac{2\pi\sqrt{(\alpha-\alpha')^2+(\beta-\beta')^2}}{\lambda}R$, we know that the intensity of the diffracted light in the focal plane of the telescope is proportional to

* André et Angot, *Annales de l'École Normale*, **10**. 323. 1881.

$$\frac{J_1^2(r)}{r^2},$$

where $J_1(r)$ denotes Bessel function of the first kind and of order 1. If the source of light be not a geometrical point, we must consider α β as variable when finding the illumination at points corresponding to α' β', and sum the effects due to all elements of the luminous plane. In other words, the illumination is proportional to

$$\int \frac{J_1^2(r)}{r^2} d\sigma$$

where $d\sigma$ represents an element of the luminous area. For effecting the integration, we can, for nearly normal incidence, assume $\alpha'=0$ $\beta'=0$, and put

$$r=\frac{2\pi R\sqrt{\alpha^2+\beta^2}}{\lambda}=\frac{2\pi RA}{\lambda}$$

A denoting the angular interval of the incident and diffracted rays. Thus, expressed in polar coordinates r, θ, the present problem reverts to the evaluation of

$$\iint \frac{J_1^2(r)}{r} dr d\theta$$

the integration extending over the whole luminous source. It is to be remarked that, for $\lambda=0.589\ \mu$, $r=1$, $A=1''$, the value of $R=1.93$ cm.

The intensity of illumination is consequently given by

$$I=K\iint \frac{J_1^2(r)}{r} dr d\theta,$$

K being a constant to be afterwards determined.

Since

$$-\frac{1}{2}\frac{d}{dr}\left\{J_0^2(r)+J_1^2(r)\right\}=\frac{J_1^2(r)}{r}\,*,$$

we can write

$$I=-\frac{K}{2}\iint \frac{d}{dr}\left\{J_0^2(r)+J_1^2(r)\right\} dr d\theta$$

* Lommel, *Mathematische Annalen*, **14**, 1879.
Rayleigh, *Phil. Mag.*, **11** (5), 1881.

If the luminous source be an infinitely large plane,

$$I_\infty = -K.\pi$$

since $J_0(0)=1$, $J_1(0)=0$, $J_0(\infty)=0$, $J_1(\infty)=0$.

We shall henceforth assume the intensity for an infinite plane to be unity, as is done by other writers; thus

$$K=-\frac{1}{\pi},$$

and

$$I=\frac{1}{\pi}\iint\frac{J_1^2(r)}{r}drd\theta \qquad (\mathrm{I})$$

Denoting the limits of integration with respect to r by r_0 and r_1, which are generally functions of θ, we obtain

$$I=\frac{1}{2\pi}\int\{J_0^2(r_0)+J_1^2(r_0)-J_0^2(r_1)-J_1^2(r_1)\}d\theta \qquad (\mathrm{II})$$

At the centre of a circular image, of radius r, the above expression reduces to

$$I=1-J_0^2(r)-J_1^2(r), \qquad (\mathrm{II}_a)$$

and at the vertex of a circular sector including angle α to

$$I=\frac{\alpha}{2\pi}\left\{1-J_0^2(r)-J_1^2(r)\right\}. \qquad (\mathrm{II}_b)$$

§ 2. Curve $y=J_0^2(x)+J_1^2(x)$

Before entering into further discussion it will be worth while to examine the term $J_0^2(r)+J_1^2(r)$ which enters into the expression for the intensity of the diffracted light.

Although the values of $J_0^2(r)$ and $J_1^2(r)$ are in themselves oscillating, the sum of these two functions presents a remarkable aspect, as will be easily seen by representing it as a curve

$$y=J_0^2(x)+J_1^2(x).$$

In the first place, y cannot be negative, so that the curve is confined to the positive part of the ordinate; in the second place the relation

$$J_0^2(x)+2J_1^2(x)+2J_2^2(x)+2J_3^2(x)+\ldots\ldots\ldots\ldots=1$$

shows that y cannot be greater than 1, which it will attain only for $x=0$.

Since

$$\frac{dy}{dx} = -2\frac{J_1^2(x)}{x},$$

and

$$\frac{d^2y}{dx^2} = -2\frac{J_1(x)}{x}\left\{2J_0(x) - \frac{3J_1(x)}{x}\right\},$$

we see that points corresponding to the roots x_n of $J_1^2(x)=0$ are the points of inflexion and have tangents parallel to the x axis. The coordinates of these points are x_n, $J_0^2(x_n)$.

From the nature of the roots of $J_1(x)=0$, we see that these points occur at nearly equal intervals of the abscissæ little greater than π, to which the interval will gradually approximate with increasing values of x_n; consequently the curve has neither maximum nor minimum (excepting the point $x_0=0$, $y=1$), but has an infinite number of inflexional tangents parallel to the x axis.

In addition to these, we find another series of inflexion points given by the equation

$$\frac{3J_1(x)}{x} = 2J_0(x);$$

or, since

$$\frac{2J_1(x)}{x} = J_0(x) + J_2(x)$$

the above equation can also be written

$$\frac{J_0(x)}{J_2(x)} = 3$$

For any value of x, $J_1(x)<1$, the relation to be satisfied at the inflexion points

$$\frac{J_1(x)}{J_0(x)} = \frac{2x}{3}$$

shows that for large values of x, $J_0(x)$ must be very small; thus the abscissæ of inflexion points belonging to this set will ultimately be coincident with the roots of

$$J_0(x) = 0.$$

These inflexion points are nearly coincident with the maximum or minimum position of $J_1(x)$. If in the above equation $J_0(x)$ and $J_1(x)$ be expanded in semi-convergent series, we get the equation

$$tg\left(x-\frac{\pi}{4}\right)=\frac{8}{11}x-0.5392\frac{1}{x}+0.603\frac{1}{x^3}-\ldots\ldots\ldots$$

The ordinates of these inflexion points are given by

$$y=J_1^2(x)\left(1+\frac{9}{4x^2}\right)$$

We shall distinguish the inflexion points given by the roots of $J_1(x)=0$ from those given by $\frac{J_0(x)}{J_2(x)}=3$ by calling the former inflexion points of the first set and the latter those of the second set. The above considerations show that the inflexion points of the second set lie nearly midway between those of the first set, the approximation becoming closer for increasing values of x.

Between the inflexion points of the two sets, there must be points of maximum curvature; these points are evidently given by

$$J_0^2(x)-J_1^2(x)-\frac{5J_0(x)\,J_1(x)}{x}-\frac{2J_1^2(x)}{x^2}\left[3+2J_1^4(x)+4J_0^2(x)\,J_1^2(x)\right]$$
$$+16\,\frac{J_0(x)\,J_1^5(x)}{x^3}-51\frac{J_1^6(x)}{x^4}=0$$

If x be large, the leading term is evidently $J_0^2(x)-J_1^2(x)$, while the remaining terms decrease very rapidly with increasing values of x; thus the points of maximum curvature will be approximately given by

$$J_0(x)=\pm J_1(x)$$

This equation shows that these points lie nearly midway between the inflexion points of the first and of the second set. Thus, if the successive inflexion points of the first set be joined by a series of

straight lines, one part of the curve will lie to the right and the other to the left of the line ; the points of intersection of the line with the curve will, for large values of x, lie nearly midway between the two points and nearly coincident with the inflexion points of the second set.

Represented graphically, the curve shows a succession of steps, at nearly equal horizontal intervals ; the height of the consecutive steps becomes smaller and the rate of decrease diminishes, as we recede further from the axis of y.

Fig. 1. Pl. XVI. shows the curve from $x=0$ to $x=10$; for larger values of x, the curve is given in Fig. 2. The positions of the inflexion points of the 1st set are given by the intersection of the two dotted lines, of which the one represents the inflexional tangents and the other the abscissæ of the inflexion points.

It will be further shown that the mean curve is approximately a rectangular hyperbola.

$$xy=\frac{2}{\pi}$$

§ 3. Expressions for $J_0^2(x)+J_1^2(x)$

Different expressions can be found for y. For small values of x, we may expand it in powers of x, by means of well-known definite integrals

$$J_0^2(x)=\frac{1}{\pi}\int_0^\pi J_0(2x\,sin\omega)d\omega\,,$$

$$J_1^2(x)=\frac{1}{\pi}\int_0^\pi J_0(2x\,sin\omega)cos\,2\omega\,d\omega\,,$$

or

$$J_0^2(x)+J_1^2(x)=\frac{2}{\pi}\int_0^\pi J_0^2(2x\,sin\omega)cos^2\omega\,d\omega\,;$$

whence by expanding $J_0(2x \sin \omega)$ in powers of $2x \sin \omega$ and integrating, we obtain

$$J_0^2(x)+J_1^2(x)=\sum \frac{(-1)^n \Pi(2n)}{2^{2n+1}[\Pi(n)]^3 \Pi(n+1)} x^{2n} \qquad (A)$$

This series converges very slowly for values of x little over unity; in place of the ascending series, we may conveniently employ the following semi-convergent series, which can be easily arrived at from the corresponding expansions of $J_0^2(x)$ and $J_1(x)$. Thus

$$J_0^2(x)=\frac{1}{\pi x}\left(1-\frac{1}{8x^2}+\sin 2x-\frac{\cos 2x}{4x}-\frac{5\sin 2x}{32x^2}+\cdots\cdots\cdots\right),$$

$$J_1^2(x)=\frac{1}{\pi x}\left(1+\frac{3}{8x^2}-\sin 2x-\frac{3}{4}\frac{\cos 2x}{x}-\frac{3}{32}\cdot\frac{\sin 2x}{x^2}+\cdots\cdots\cdots\right)$$

whence

$$J_0^2(x)+J_1^2(x)=\frac{2}{\pi x}\left(1+\frac{1}{8x^2}-\frac{\cos 2x}{2x}-\frac{\sin 2x}{8x^2}+\cdots\cdots\cdots\right) \qquad (B)$$

The above series is rapidly convergent, and can be conveniently used for values of x greater than the first root $x_1=3.8317$ of $J_1(x)=0$; at the last mentioned value of x, the number obtained for $J_0^2(x)+J_1^2(x)$ will be accurate to the fourth decimal place.

In the neighbourhood of the inflexion points of the first set, the value of y remains nearly constant; we can thus expand $J_0^2(x)+J_1^2(x)$ in Maclaurin's series. Denoting the roots of $J_1(x)=0$ by $x_0, x_1, x_2 \ldots\ldots$, and putting $y_n=J_0^2(x_n)$, $\xi=x-x_n$, we shall obtain the following series for y in the neighbourhood of the point x_n, y_n

$$y=J_0^2(x_n)\left\{1+*+*-\frac{4}{3!}\frac{\xi^3}{x_n}+\frac{12}{4!}\frac{\xi^4}{x_n^2}-\frac{4}{5!}\left(\frac{39}{x_n^2}-4\right)\frac{\xi^5}{x_n}+\ldots\ldots\right\} \qquad (C)$$

Of these three expressions, we shall have occasion to use the form (B) most frequently, as it expresses the nature of the curve

$y=J_0^2(x)+J_1^2(x)$ in the simplest manner. It shows that the curve is to the first approximation a rectangular hyperbola.

$$xy=\frac{2}{\pi}, \qquad (D)$$

if x be not very small. To the second approximation, we shall have to introduce the term $\frac{\cos 2x}{x^2}$, which gives the curve an undulating appearance; the effect of the third and fourth terms is still smaller, so that for practical purposes, it is sufficient to assume the mean curve to be a hyperbola, as it is almost useless to push the calculation to the fourth decimal place. To show the difference in y_n calculated from (13) and from (D), I give the following table:

x	*calculated from* (B)	*calculated from* (D)
$x_1=3.832$	$y_1=0.1622$	$y_1=0.1661$
$x_2=7.016$	$y_2=0.0901$	$y_2=0.0907$
$x_3=10.173$	$y_3=0.0624$	$y_3=0.0626$
$x_4=13.324$	$y_4=0.0477$	$y_4=0.0478$

Thus the coincidence becomes closer with increasing values of x.

§ 4. Intensity at the centre of a circular disc.

Equation (II_a) § 1. shows that the intensity of light at the centre of a luminous disc as observed through a telescope is given by

$$I= 1-J_0^2(r)-J_1^2(r).=1-y$$

If the luminous disc be divided by a series of concentric circles of radius x_n into a number of zones whose breadth is equal to the difference between the successive roots of $J_1(x)=0$, we find that the illumination at the centre due to each of these zones is given by the height of the corresponding step in the curve $y=J_0^2(x)+J_1^2(x)$. The diminution in the height of these steps with increasing x shows that the

effect of the zone of nearly the same breadth varies almost inversely as its distance from the centre. The same reasoning will apply to a circular sector. The following tables give the intensity at the centre of luminous discs whose radii are equal to the roots of $J_1(x)=0$. It will be found from the table that the effect of the first zone is 5 times greater than that of all the rest combined. Thus the illumination at the centre of a luminous circular disc of small radius will not sensibly differ from that of infinite extent. We shall have occasion to discuss the illumination of the disc whose radius is less than x_1 in a subsequent section.

n	x_n	$1-y_n=I_n$	I_n-I_{n-1}
0	0.00000	0.00000	
1	3.83171	0.83778	0.83778
2	7.01559	0.90994	0.07216
3	10.17347	0.93765	0.02771
4	13.32369	0.95232	0.01467
5	16.47063	0.96140	0.00908
6	19.61586	0.96758	0.00618
7	22.76008	0.97205	0.00447
8	25.90367	0.97544	0.00339
9	29.04683	0.97809	0.00265
10	32.18968	0.98023	0.00214
11	35.33231	0.98199	0.00176
12	38.47477	0.98346	0.00147
13	41.61709	0.98471	0.00125
14	44.75932	0.98578	0.00107
15	47.90146	0.98671	0.00093
16	51.04354	0.98753	0.00082
17	54.18555	0.98825	0.00072
18	57.32753	0.98890	0.00064
19	60.46946	0.98947	0.00058

n	x_n	$1-y_n=I_n$	I_n-I_{n-1}
20	63.61136	0.98999	0.00052
21	66.75323	0.99046	0.00047
22	69.89507	0.99089	0.00043
23	73.03690	0.99128	0.00039
24	76.17700	0.99164	0.00036
25	79.32049	0.99197	0.00033
30	95.02923	0.99330	0.00023
40	126.44614	0.99497	0.00013
50	157.86266	0.99597	0.00008

The foregoing table enables us to integrate (II) mechanically for a source of given geometrical shape. About a point at which the intensity is sought describe a number of concentric circles dividing the region of integration into a series of zones, whose breadth will be equal to the difference between the successive roots of $J_1(x)=0$. If the angle subtended at the point by these zones be known, we can by summation of the separate effects find the intensity at the required point.

If the luminous source subtend several seconds of arc, the value of r would be a large quantity. Thus, if the boundary does not show great irregularities, we can approximately assume it to be straight for contiguous zones. Calculating the mean angle x_n subtended by the zone at the point, we get approximately

$$I=\frac{1}{2\pi}\sum a_n(I_n-I_{n-1}). \qquad \text{(III)}$$

We notice that for the first zone, $I_1-I_0=0.8378$, while for all the rest $I_\infty-I_1=0.1622$; it is thus necessary to subdivide the first zone into a series of subsidiary zones and sum their effect as for the other zones, provided a is different from 2π. In addition to this, we shall have to add a small correction for a few successive zones, inasmuch as we multiply the height of the step by the arithmetical mean of the

limiting angles of the zones, instead of taking some other proper value of a_n, which will exactly give the illumination due to the zone considered.

The correction is calculated in the following way. Let $r_1=0A$ and $r_2=0B$ represent the radii of the circles bounding a zone; consider the outer edge AB of the zone to be straight, and that we have for the effect of the zone the expression $\frac{\vartheta}{2\pi}\{J_0^2(r_2)+J_0^2(r_1)\}$ where ϑ is the angle subtended at the given point by a circular arc described with radius $0M=\frac{r_1+r_2}{2}=r_0$, and included between the edges of the zone. The correction to be applied in the above expression is evidently the difference in the illumination due to AEM and BDM. Writing this I'_1 and I'_2, we have

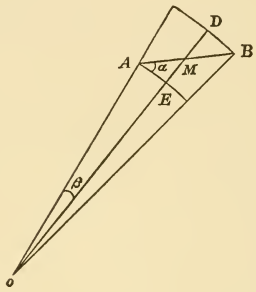


Fig. I.

$$I'_1=\frac{1}{\pi}\int_0^\beta\int_{r_0-\delta}^{r_0}\frac{J_1^2(r)}{r}dr\,d\vartheta\ ,$$

where

$$\delta=r_0 tg\,a\,.\,\vartheta\ ,$$

$$r_0\beta=\frac{r_2-r_1}{2}tg\,a.$$

Similary

$$I'_2=\frac{1}{\pi}\int_0^\beta\int_{r_0}^{r_0+\delta}\frac{J_1^2(r)}{r}dr\,d\vartheta\ ,$$

whence we obtain

$$I'_1-I'_2=\frac{1}{2\pi}\int_0^\beta\Big\{J_0^2(r_0+\delta)+J_1^2(r_0+\delta)+J_0^2(r-\delta)+J_1^2(r_0-\delta)-2J_0^2(r_0)-2J_1^2(r_0)\Big\}d\vartheta$$

$$=\frac{1}{2\pi}\int_0^\beta\Big\{y_{(r_0+\delta)}+y_{(r_0-\delta)}-2y_{r_0}\Big\}d\vartheta$$

Expanding the expression within the parenthesis, we obtain

$$I_1'-I_1'=\frac{1}{\pi}\Big\{\frac{1}{3!}\Big(\frac{d^2y}{dr^2}\Big)_{r_0}b^2\beta^3+\frac{1}{5!}\Big(\frac{d^4y}{dr^4}\Big)_{r_0}b^4\beta^5+\ldots\ldots\Big\}$$

where

$$b=r_0 tg a.$$

The correction is very small, if a be not very small ; for the sake of convenience, I have calculated the following approximate values for the zones 2, 3, 4, 5.

Number of zones.	r_0	$\frac{1}{3!}\left(\frac{d^2y}{dr^2}\right)_{r_0}$	$\frac{1}{5!}\left(\frac{d^4y}{dr^4}\right)_{r_0}$	$\frac{1}{7!}\left(\frac{d^6y}{dr^6}\right)_{r_0}$
2	5.424	0.0054	0.00040	0.000027
3	8.595	0.0013	0.00010	0.000007
4	11.749	0.0005	0.00004	0.000003
5	14.897	0.0003	0.00002	0.000001

§ 5. Intensity at the Rim of a circular Disc.

The present problem is directly connected with the theory of astronomical instruments, and has important bearing on the observation of celestial bodies. The simplest and perhaps the most important calculation we can make is that of the case of a luminous circular disc. We have already seen how the intensity at the centre of a circular disc can be easily calculated ; we shall now proceed to the discussion of the intensity at its rim, and then obtain the result for the general case when the point lies outside or inside the image of the disc.

Let the radius of the disc be a, then the distance of a point on the periphery will be given by

$$r=2a\cos\theta$$

The intensity at the rim $r=0$ is given by

$$I=\frac{2}{\pi}\int_0^{\frac{\pi}{2}}\int_0^{2a\cos\theta}\frac{J_1^2(r}{r}dr\,d\theta$$

Integrating it first with respect to θ, we can put the integral under the form

$$I=\frac{2}{\pi}\int_0^{2a}\int_0^{arc\cos\frac{r}{2a}}\frac{J_1^2(r)}{r}dr\,d\theta$$

$$=\frac{2}{\pi}\int_0^{2a}\frac{J_1^2(r)}{(r)}arc\ cos\frac{r}{2a}.\ dr$$

Integrating by parts,

$$I=\frac{1}{2}-\frac{1}{\pi}\int^{2a}\frac{J_0^2(r)+J_1^2(r)}{\sqrt{4a^2-r^2}}dr.$$

The above integral shows that the intensity at the rim approaches $\frac{1}{2}$ as the radius of the disc is indefinitely increased.

We have already seen how $J_0^2(r)+J_1^2(r)$ can be expanded in ascending powers of r as well as in a semi-convergent series. For values of r smaller than x_1, we can not use the last mentioned series, while for values of r somewhat greater than x_1, it is disadvantageous to use the former series. We shall therefore have to divide the integral into two parts: namely, one extending from 0 to x_1, for which the expansion in ascending powers of r should be used; and the other from x_1 to $2a$, for which the semi-convergent series should be employed.

It is to be noticed that the variation of $J_0^2(r)+J_1^2(r)$ is very small in the neighbourhood of $r=x_1$, so that it would be advantageous to assume the limit of integration at $r=x_1$, in order to diminish the error in integration.

Thus,

$$I=\frac{1}{\pi}\int_0^{2a}\left(1-J_0^2(r)-J_1^2(r)\right)\frac{dr}{\sqrt{4a^2-r^2}}$$

$$=\frac{1}{2}-\frac{1}{\pi}arc\ sin\frac{x_1}{2a}+\int_0^{x_1}\frac{dr}{\sqrt{4a^2-r^2}}-\frac{1}{\pi}\int_{x_1}^{2a}\left(J_0^2(r)+J_1^2(r)\right)\frac{dr}{\sqrt{4a^2-r^2}}$$

The latter integral should again be divided into two parts, of which the one is

$$\int_0^{x_1}\left(J^2(r)+J_1^2(r)\right)\frac{dr}{\sqrt{4a^2-r^2}}=$$

$$\frac{1}{2a}\int_0^{x_1}\left((J_0^2(r)+J_1^2(r)\right)\left(1-\frac{r^2}{2.4a^2}+\frac{1.3}{2.4}\frac{r^4}{(4a^2)^2}-\ldots\ldots\right)dr,$$

whence we obtain by expansion,

$$\int_0^{x_1}\left[1-\left(J_0^2(r)+J_1^2(r)\right)\right]\frac{dr}{\sqrt{4a^2-r^2}}=\frac{0.9615}{a}+\frac{1.579}{a^3}+\frac{1.543}{a^5}$$

which converges very rapidly when a is large compared to x_1.

In the second integral, we have to put

$$J_0^2(r)+J_1^2(r)=\frac{2}{\pi r}\left(1-\frac{\cos 2r}{2r}+\frac{1-\sin 2r}{8r^2}\right)$$

Thus, we shall have to calculate the following integrals:

$$\int_{x_1}^{2a}\frac{dr}{r\sqrt{4a^2-r^2}}=-\frac{1}{2a}\log tg\frac{\vartheta_1}{2},\quad \text{where } \vartheta_1=\arcsin\frac{x_1}{2a};$$

$$\int_{x_1}^{2a}\frac{dr}{r^3\sqrt{4a^2-r^2}}=\frac{1}{8a^3}\left(\frac{\cot g\,\vartheta_1}{\sin\vartheta_1}\right)-\frac{1}{8a_3}\log tg\frac{\vartheta_1}{2},$$

and $\int_{x_1}^{2a}\frac{\cos 2r\,dr}{r^2\sqrt{4a_2-r^2}}$ and $\int_{x_1}^{2a}\frac{\sin 2r\,dr}{r^3\sqrt{4a^2-r^2}}$, of which the last two require a little consideration.

$$\int_{x_1}^{2a}\frac{\cos 2r\,dr}{r_2\sqrt{4a^2-r^2}}=\frac{1}{2}\int_{x_1}^{2a}\frac{\cos 2r}{r^3}\frac{d(r^2)}{\sqrt{4a^2-r^2}}$$

$$=\frac{1}{2}\sqrt{4a^2-x_1^2}\,\frac{\cos 2x_1}{x_1^3}+a\int\sqrt{1-\frac{r^2}{4a^2}}\,d\left(\frac{\cos 2r}{r^3}\right)$$

Expanding $\sqrt{1-\frac{r^2}{4a^2}}$ in powers of $\frac{r^2}{4a^2}$, and neglecting terms beyond $\frac{1}{a^2}$, we can find without difficulty

$$\int_{x_1}^{2a}\frac{\cos 2r\,dr}{r^2\sqrt{4a^2-r^2}}=-\frac{0.01367}{a}-\frac{3}{32}\frac{\cos 4a}{a^2}\quad\text{nearly};$$

In a similar manner

$$\int_{x_1}^{2a}\frac{\sin 2r\,dr}{r^3\sqrt{4a^2-r^2}}=\frac{0.00322}{a}-\frac{5}{16}\frac{\cos 4a}{a^2}\quad\text{nearly}.$$

Arranging the integrals in a suitable way and writing

$$\frac{1}{\pi}\ arc\ sin\frac{x_1}{2a}=\frac{0.60984}{a}-\frac{0\ 3731}{a^3}+\frac{0.6162}{a^5},$$

$$log\ tg\ \frac{1}{2}\ arc\ sin\ \frac{x_1}{2a}=\ log\ x_1-log\ 4a-\frac{x_1^2}{48a^2}-\frac{3}{128}\frac{x_1^4}{a^4},$$

we find, for the intensity at the rim of a circular disc, whose radius is large compared to x_1

$$I_R=\frac{1}{2}-\frac{log\ 4a}{\pi^2\ a}-\frac{0.1654}{a}+0.016\ \frac{cos\ 4a}{a^2}\quad \text{nearly.}\quad \text{(IV)}$$

As was before remarked, the intensity at the rim approaches $\frac{1}{2}$ with increasing values of a ; it is moreover seen how the fluctuation due to the term $cos\ 4a$ is negligibly small. By applying the above formula, the following table was calculated for $a>20$.

a	I_R	a	I_R
20	0.4695	300	0.4971
25	0.4747	400	0.4977
30	0.4782	500	0.4981
35	0.4809	600	0.4984
40	0.4830	700	0.4986
45	0.4846	800	0.4988
50	0.4860	900	0.4989
60	0.4880	1000	0.4990
70	0.4895	1500	0.4993
80	0.4906	2000	0.4995
90	0.4915	2500	0.4996
100	0.4923	3000	0.4996
150	0.4946	∞	0.5000
200	0.4958		
250	0.4965		

§ 6. Intensity at any Point of the Focal Plane due to a Circular Source of Light.

Let us next find the intensity of light at any point 0 in the focal plane of the telescope, where 0 may lie either external or internal to the image of the circular source. Put angle $BCP=2\varphi$, angle $BOP=\theta$, and $AO=\delta$, AOB being the diameter passing through the given point 0 ;

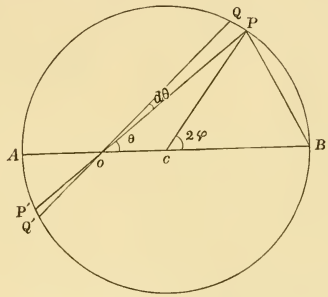
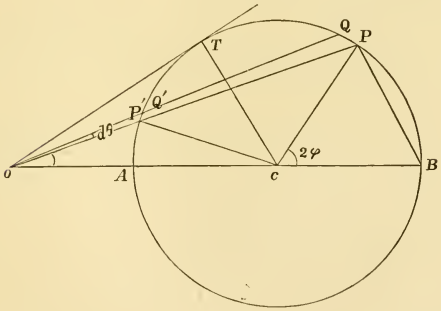


Fig. 2.



Then $$OP^2=\rho^2=(a-\delta)^2+a^2+2a(a-\delta)\cos 2\varphi$$
$$=(2a-\delta)^2-4a(a-\delta)\sin^2\varphi\,,$$

Thus $$\rho_i=(2a-\delta)\sqrt{1-k_i^2\sin^2\varphi}\,,\ \text{where } k_i^2=\frac{4a(a-\delta)}{(2a-\delta)^2}$$

when 0 lies within the circle ; similarly

$$\rho=(2a+\delta)\sqrt{1-k_e^2\,sin^2\varphi}\,,\quad \text{where } k_e^2=\frac{4a(a+\delta)}{(2a+\delta)^2}$$

when 0 lies external to the circle. We see from the expression for k_i and k_e that both are smaller than 1.

We can easily prove that

$$d\theta=\left(1+\frac{\delta}{(2a-\delta)\,(1-k_i^2\,sin^2\,\varphi)}\right)d\varphi\ *$$

$$=\left(1+\frac{k'_i}{(1-k_i^2\,sin^2\,\varphi)}\right)d\varphi \text{ for an internal point ;}$$

$$\left(k'_i=\sqrt{1-k_i^2}=\frac{\delta}{2a-\delta}\right)$$

and

$$d\theta=\left(1-\frac{k_e'}{(1-k_e\,sin^2\varphi)}\right)d\varphi \text{ for an external point ;}$$

$$\left(k'_e=\sqrt{1-k_e^2}=\frac{\delta}{2a+\delta}\right)$$

The intensity at an external point becomes

$$I_i=\frac{1}{\pi}\int_0^{2\pi}\int_0^{\rho i}\frac{J_1^2(r)}{r}\,dr d\theta$$

$$=\frac{1}{\pi}\int_0^{\pi}(1-J_0^2(\rho_i)-J_1^2(\rho_i))\,d\theta$$

$$=1-\frac{1}{\pi}\int_0^{\frac{\pi}{2}}(1-J_0^2(\rho_i)+J_1^2(\rho_i))\left(1+\frac{k'}{1-k_i^2\,sin^2\,\varphi}\right)d\varphi.$$

At an external point

$$I_e=\frac{1}{\pi}\int_{-\alpha}^{+\alpha}\int_{\rho'}^{\rho}\frac{J_1^2(r)}{r}\,dr\,d\theta$$

where $\rho'=op'$, $\rho=op$, and $\alpha=\angle AOT$.

Putting the values for ρ and θ, we obtain for

$$I_e=\frac{1}{\pi}\int_0^{\pi}(J_0^2(\rho_e)+J_1^2(\rho_e))\left(1-\frac{k'_e}{1-k_e'^2\,sin^2\varphi}\right)d\varphi.$$

If the point 0 be not very near the rim of the circle

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* See Halphen, *Fonctions Elliptiques*, Tom. 1, Chap. 1.

$$J_0^2(\rho)+J_1^2(\rho)=\frac{2}{\pi\rho} \text{ nearly,}$$

whence

$$I_i=1-\frac{2}{\pi^2(2a-\delta)}\int^{\frac{\pi}{2}}\left(1+\frac{k_i'}{1-k_i^2\sin^2\varphi}\right)\frac{d\varphi}{\sqrt{1-k_i^2\sin^2\varphi}}$$

$$=1-\frac{2}{\pi^2(2a-\delta)}\left(\frac{E}{k'_i}+K\right) \qquad \text{(V)}$$

and

$$I_e=\frac{2}{\pi^2(2a+\delta)}\int_0^{\frac{\pi}{2}}\left(1-\frac{k'_e}{1-k_e^2\sin^2\varphi}\right)\frac{d\varphi}{\sqrt{1-k_e^2\sin^2\varphi}}$$

$$=\frac{2}{\pi^2(2a+\delta)}\left(\frac{E}{k'_e}-K\right) \qquad (\text{V}_a)$$

The calculation of these complete elliptic integrals can be effected in the following manner.

Putting $l=\frac{1-\sqrt{k'}}{1+\sqrt{k}}$, $l_1=\frac{1-\sqrt{k}}{k+\sqrt{k}}$, $h=e^{-\frac{\pi K'}{K}}$,

$$h=\frac{l}{2}+2\left(\frac{l}{2}\right)^5+15\left(\frac{l}{2}\right)^9+\ldots\ldots\ldots\ldots$$

$$h_1=\frac{l_1}{2}+2\left(\frac{l_1}{2}\right)^5+15\left(\frac{l_1}{2}\right)^9+\ldots\ldots\ldots\ldots$$

with the relation $\log h \,.\, \log h_1=\pi^2$, we have

$$K=\frac{\pi}{2}(1+2h+2h^4+2h^9+\ldots\ldots\ldots\ldots)$$

$$E=k'^2K+\frac{2\pi^2}{K}\,\frac{h+4h^4+9h^9+\ldots\ldots}{1+2h+2h^4+2h^9+\ldots\ldots},$$

$$=K-\frac{2\pi^2}{K}\,\frac{h-4h^4+9h^9-\ldots\ldots}{1-2h+2h^4-2h^9+\ldots\ldots},$$

$$=\frac{\pi^2}{4K}\,\frac{1+3^2h^{1.2}+5^2h^{2.3}+\ldots\ldots}{1+h^{1.2}+h^{2.3}+\ldots\ldots\ldots}\ *,$$

Either of these formulæ enables us to calculate E from K; the intensity of illumination can therefore be easily calculated for both cases.

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* See Weierstrass-Schwarz, '*Formeln und Lehrsätze zum Gebrauche der elliptischen Functionen* 2te *Auflage*, Berlin, 1893—p. 44, p. 61.

The following table gives the values of $\frac{E}{k'}+K$ and $\frac{E}{k'}-K$.

k	$\frac{E}{k'}+K$	$\frac{E}{k'}-K$
0.1	3.1496	0.0000
0.2	3.1738	0.0001
0.3	3.2168	0.0009
0.4	3.2831	0.0031
0.5	3.3802	0.0088
0.6	3.5032	0.0196
0.7	3.7453	0.0511
0.8	4.1226	0.1328
0.9	4.9696	0.4080

The formulæ given above apply only to points far from the edge of the circular image. The most interesting case connected with the present problem is the investigation of the intensity at points in the very neighbourhood of the geometrical rim, where under certain circumstances the well-known phenomenon of drop-formation makes its appearance. As the semi-convergent expression for $J_0^2(\rho)+J_1^2(\rho)$ is no longer available in the neighbourhood of the rim, we shall have recourse to another method of integration for that portion of the region, where $J_0^2(\rho)+J_1^2(\rho)$ must be expanded according to ascending powers of ρ.

For this purpose, we shall divide the region of integration into two parts by describing a circle with radius x_1 about the point where the intensity is sought; at points of the periphery not included within the circle thus described, we can use the semi-convergent expression and apply the method of integration given above, while in the interior we have to proceed in the following manner.

As the point lies very near the periphery, δ is a very small quantity and k is very near unity; whence, if ρ be expressed in terms of

φ, φ is very nearly a right angle for points of the periphery included within the circle AB.

Let $\varphi = \frac{\pi}{2} - \psi$, where ψ is a very small angle, then

$$1 - k^2 \sin^2 \varphi = \sqrt{k'^2 + k^2\psi^2 - k^2 \frac{\psi^4}{3}} \text{ nearly.}$$

Denoting the angle subtended by AB at the centre of the circular image by $4\,\psi_1$, we obtain by the formula already given

$$\left(\frac{x_1}{2a-\delta}\right)^2 = k'^2 + k^2\left(\psi_1^2 - \frac{\psi_1^4}{3}\right).$$

Expressing k' in terms of a and δ, we obtain

$$\psi_1^2 - \frac{\psi_1^4}{3} = \frac{x_1^2 - \delta^2}{4a(a-\delta)}.$$

Practically a is a large quantity and ψ_1 a very small angle, so that we may safely neglect $\frac{\psi_1^4}{3}$, and put

$$\psi_1^2 = \frac{x_1^2 - \delta^2}{4a(a-\delta)},$$

and for points on the periphery AB

$$\rho = (2a-\delta)\sqrt{k'^2 + k^2\psi^2}$$

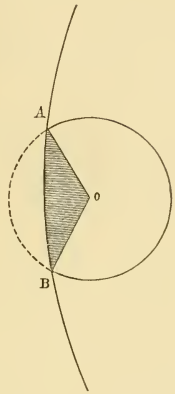


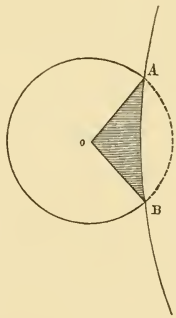
Fig. 3.

Writing $\xi = \sqrt{4a(a-\delta)}\,\psi$,

$\xi_1 = \sqrt{4a(a-\delta)}\,\psi_1 = x_1^2 - \delta^2$ nearly, we get

$$\rho = \sqrt{\delta^2 + \xi^2}$$

and $d\rho = -d\psi = \frac{d\xi}{\sqrt{4a(a-\delta)}}$



Returning to formula (II) §1, we find the intensity at 0 due to the sector OAB

$$I_s = \frac{1}{\pi}\int_0^{\alpha}\left(1 - J_0^2(\rho) - J_1^2(\rho)\right) d\theta,$$

where 2α is the angle subtended by the arc AB at 0,

$$=\frac{a}{\pi}-\frac{1}{\pi}\int_0^a\Big(J_0^2(\rho)+J_1^2(\rho)\Big)d\theta.$$

Writing the integral in the form given by the above process of reduction, we obtain

$$I_s=\frac{a}{\pi}-\frac{1}{\pi}\int_0^{\xi_1}\Big(J_0^2(\sqrt{\delta^2+\xi^2})+J_1^2(\sqrt{\delta^2+\xi^2})\Big)\Big(1+\frac{\delta(2a-\delta)}{\delta^2+\xi^2}\Big)\frac{d\xi}{\sqrt{4a(a-\delta)}},$$

$$=\frac{a}{\pi}-\frac{I_s'}{2\sqrt{a(a-\delta)}}-I_s'' \quad \text{nearly.}$$

where

$$I_s'=\frac{1}{\pi}\int_0^{\sqrt{x_1^2-\delta^2}}\{J_0^2(\sqrt{\delta^2+\xi^2})+J_1^2(\sqrt{\delta^2+\xi^2})\}d\xi \quad ,$$

$$I_s''=\frac{\delta}{\pi}\int_0^{\sqrt{x_1^2-\delta^2}}\frac{J_0^2(\sqrt{\delta^2+\xi^2})+J_1^2(\sqrt{\delta^2+\xi^2})}{\delta^2+\xi^2}d\xi \ .$$

When the point 0 is external to the circle

$$-I_s'=\frac{a}{\pi}-\frac{I_s'}{2\sqrt{a(a-\delta)}}+I_s''$$

Gauss's method of mechanical quadrature seems specially suited for calculating the two integrals I_s' and I_s''. Assuming $n=3$ in the usual formula, the error of approximation will in the present case scarcely affect the fourth decimal place. The course of I_s' and I_s'' is shown in Fig's 3 and 4 (Plate XVI & XVII). If greater accuracy be desired, we must assume the values of n greater than 3; to facilitate the calculation, I have calculated a table* (see Appendix) of $J_0^2(x)+J_1^2(x)$ for values of x ranging from 0 to 3.83. The table gives, as was already noticed, the intensity at the centre of a circular image, whose radius is x, if the number given in the table be subtracted from 1.

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* For the construction of the table, I am indebted to Mr. S. Miyazaki; the following errors were noticed in Meissel's 'Tafel der Bessel'schen Functionen.'

$k=0.62$	$J_0(k)=0.9061843$	instead of	0.9051843
$k=1.71$	$J_0(k)=0.3922044$	,, ,,	0.3932044
$k=1.89$	$J_0(k)=0.2876313$	,, ,,	0.2866313

The value of $J_0(1.71)$ was corrected by Meissel, as reprinted in Gray-Matthew's 'Treatise on Bessel Functions.'

The effect due to the remaining part of the circular source can be easily calculated by adopting the semi-convergent series for $J_0^2(\rho)+J_1^2(\rho)$. Retaining the first term only, we get for the illumination at an internal point 0 due to the part external to the sector.

$$I'_i=\frac{\pi-a}{\pi}-\frac{2}{\pi^2(2a-\delta)}\int_0^{\varphi_1}\left(1+\frac{k'_i}{1-k_i^2\,sin^2\varphi}\right)\frac{d\varphi}{\sqrt{1-k_i^2\,sin^2\,\varphi}}$$

$$=\frac{\pi-a}{\pi}-\frac{2}{\pi^2(2a-\delta)}\left(\frac{E(\varphi_1)}{k_i'}+F(\varphi_1)-\frac{k_i^2}{2k_i'}\,\frac{sin\,2\varphi_1}{\sqrt{1-k_i^2\,sin^2\varphi_1}}\right)$$

where $F(\varphi_1)$ and $E(\varphi_1)$ denote elliptic integrals of the 1st and 2nd kind respectively.

For an external point, we shall have

$$I'_e=\frac{a}{\pi}+\frac{2}{\pi^2(2a-\delta)}\left(-\frac{E(\varphi_1)}{k'_e}+F(\varphi_1)+\frac{k_e^2}{2k_e}\,\frac{sin\,2\varphi_1}{\sqrt{1-k_e^2\,sin^2\varphi_1}}\right)$$

Thus by the addition of these separate effects, we obtain the expression for the intensity of illumination at an external point in the very neighbourhood of the rim.

$$I_i=I_i'+I_s$$

$$=1-\frac{2}{\pi^2(2a-\delta)}\left(\frac{E(\varphi_1)}{k'_i}+F(\varphi_1)-\frac{k_i^2}{2k'_i}\,\frac{sin\,2\varphi_1}{\sqrt{1-k^2\,sin^2\varphi_1}}\right)$$

$$-\frac{I'_s}{2\sqrt{a(a-\delta)}}-I_s''. \qquad \text{(VI)}$$

At an external point

$$I_e=I'_e+I_{s'}=\frac{2}{\pi^2(2a-\delta)}\left(-\frac{E(\varphi_1)}{k_e'}+F(\varphi_1)+\frac{k_e^2}{2k_e'}\,\frac{sin\,2\varphi_1}{\sqrt{1-k_e^2\,sin\varphi_1}}\right)$$

$$+\frac{I'_{s'}}{2\sqrt{a(a-\delta)}}-I_s''. \qquad \text{(VI}_a\text{)}$$

The expression within the brackets can be calculated by means of Legendre's tables for the two integrals E and F. The course of the function for different values of φ_2 and $\frac{\delta}{2a}$ is shown in Fig. 5 Pl. XVII,

of which the right side applies to I_i (inside the circle) and that to the left to I_e (external to the circle).

Having found the values of these different integrals, we are now in a position to discuss the illumination near the rim of the circular image.

We have already found that the intensity of light at the centre of a circular disc is nearly equal to unity when the diameter is tolerably large, and at the rim nearly equal to half the intensity at the centre. As will be seen from the expression for I_i, the intensity increases very rapidly from the rim towards the centre, and from that for I_e, decreases very rapidly as we pass from the rim outwards. In fact the variation of intensity is greatest near the rim, the change however not taking place abruptly but fading away gradually, as illustrated in Fig. 6 Pl. XVII, in which the dark line refers to $a=\infty$ and the dotted line to $a=40$. The image of a luminous disc as seen through a telescope is thus not sharply defined, as the intensity at the geometrical rim changes continuously. If the intensity for the limit of visibility be less than I_R, the image of the disc will appear to a slight extent broadened.

§ 7. Lines of Equal Intensity.

For practical purposes, it is sometimes convenient to draw the lines of equal intensity. For a circular disc, they consist of a series of concentric circles, which drawn for equal differences of intensity crowd together near the geometrical edge. When there are different sources of light, we can superpose the separate effects and graphically represent the distribution of intensity in the following manner.

Draw the lines of equal intensity for the image of each source, and at the point of intersection of any two lines, the intensity will be the sum of the two. We thus obtain a system of points of equal intensity. By

drawing the lines at small intervals, we can obtain a sufficiently large number of such points. The curve obtained by joining these points will be that of equal intensity, and will represent the distribution due to these different sources. The process of drawing the lines of equal intensity is thus analogous to that of drawing equipotential lines. In Fig. 7. Pl. XVII., the fine lines are those of equal intensity for a circular disc of radius 40, and an infinite plane with a straight edge; the combined effect due to the luminous plane and the dark disc is illustrated by the distribution of thick lines, which give the places of equal intensity. The dotted lines show the geometrical boundary of the plane and the disc.

A problem which has been the subject of long discussion by astronomers comes next under our notice. In the transit of inferior planets over the sun's disc, we observe the phenomenon of drop-formation by the ingress or egress between the rim of the sun and of the planet.

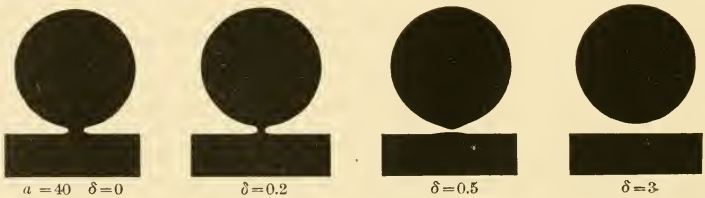
Suppose now that the luminous source is a circular disc, on which there is a small dark circular space nearly touching the rim of the disc. The image as seen through the telescope will form a drop near the rim, as consideration of the lines of equal intensity will immediately show. We can imagine such a source as produced by the superposition of two different sources, one of which consists of a circular disc of uniform intensity without any dark space, while the other consists of a circular disc occupying the place of the dark space, and of such an intensity that it is *equal* but of *opposite* sign. This consideration gives the solution of the problem either as a mathematical formula or as a graphical representation.

For the latter purpose, we draw the concentric circles representing lines of equal intensity for the luminous source, and similar lines of equal *negative* intensity for the imaginary source occupying the

dark space; we shall by the above described process be able to obtain a series of lines of equal intensity due to these sources. In the diagrams (Figs. 8 and 9 Pl. XVII) I give a portion of these lines in the immediate neighbourhood of the rim of the luminous source ($a=\infty$) when there is a dark circular space ($a=40$); the lines are drawn for the same difference 0.1 of the intensity. Fig. 8 represents the lines when the dark disc touches the rim, and Fig. 9 when the nearest distance δ between the rim is 1. In both figures, the boundaries of the luminous source are shown by dotted lines.

The inspection of these figures shows that when the dark space is in geometrical contact with the rim of the luminous source, it appears only as a dark protuberance from the surrounding dark space into the luminous source; with the receding of the dark space towards the interior of the luminous source, the connecting ligament becomes thinner and finally falls away. The inner dark space is a little elongated and assumes a pear-shaped appearance, while the external dark space bulges out towards the luminous source. The change is however transient; with further ingress, the dark disc becomes circular and the swelling of the external dark space vanishes away. It must not be forgotten that the image of the dark disc is generally less than actually would be the case, and the edge of the luminous source will extend a little into the dark space. To show the successive stages of these protruding dark discs, I give the following diagrams (Fig. 4),

Fig. 4.



$a=40$ $\delta=0$ $\delta=0.2$ $\delta=0.5$ $\delta=3$

which approximately represent the appearance of such a dark disc seen within the luminous source, as observed by means of a telescope.

We have thus arrived at the probable explanation of the drop-formation during the transit of inferior planets. If the dark space be taken nearly equal to the luminous source and have small protuberances, we can by a similar process obtain a result, which has close analogy with Baily's beads, observed during the solar eclipse.

$$y = J_0^2(x) + J_1^2(x)$$

x	y	x	y	x	y
0.00	1.00000	0.40	0.96080	0.80	0.85225
0.01	0.99998	0.41	0.95884	0.81	0.84883
0.02	0.99990	0.42	0.95685	0.82	0.84538
0.03	0.99978	0.43	0.95484	0.83	0.84191
0.04	0.99960	0.44	0.95275	0.84	0.83842
0.05	0.99939	0.45	0.95063	0.85	0.83490
0.06	0.99910	0.46	0.94849	0.86	0.83134
0.07	0.99879	0.47	0.94627	0.87	0.82777
0.08	0.99840	0.48	0.94402	0.88	0.82416
0.09	0.99799	0.49	0.94175	0.89	0.82055
0.10	0.99750	0.50	0.93942	0.90	0.81688
0.11	0.99698	0.51	0.93704	0.91	0.81322
0.12	0.99640	0.52	0.93465	0.92	0.80951
0.13	0.99578	0.53	0.93219	0.93	0.80580
0.14	0.99512	0.54	0.92971	0.94	0.80205
0.15	0.99438	0.55	0.92717	0.95	0.79830
0.16	0.99362	0.56	0.92460	0.96	0.79452
0.17	0.99281	0.57	0.92200	0.97	0.79070
0.18	0.99194	0.58	0.91935	0.98	0.78687
0.19	0.99102	0.59	0.91667	0.99	0.78303
0.20	0.99004	0.60	0.91394	1.00	0.77917
0.21	0.98904	0.61	0.91120	1.01	0.77529
0.22	0.98798	0.62	0.90839	1.02	0.77139
0.23	0.98686	0.63	0.90557	1.03	0.76747
0.24	0.98570	0.64	0.90269	1.04	0.76354
0.25	0.98450	0.65	0.89979	1.05	0.75960
0.26	0.98324	0.66	0.89685	1.06	0.75562
0.27	0.98194	0.67	0.89387	1.07	0.75164
0.28	0.98060	0.68	0.89087	1.08	0.74764
0.29	0.97920	0.69	0.88783	1.09	0.74364
0.30	0.97776	0.70	0.88475	1.10	0.73960
0.31	0.97627	0.71	0.88165	1.11	0.73557
0.32	0.97472	0.72	0.87850	1.12	0.73152
0.33	0.97314	0.73	0.87533	1.13	0.72746
0.34	0.97152	0.74	0.87211	1.14	0.72338
0.35	0.96984	0.75	0.86888	1.15	0.71929
0.36	0.96812	0.76	0.86562	1.16	0.71520
0.37	0.96636	0.77	0.86232	1.17	0.71108
0.38	0.96454	0.78	0.85899	1.18	0.70698
0.39	0.96268	0.79	0.85564	1.19	0.70284

$$y = J_0^2(x) + J_1^2(x)$$

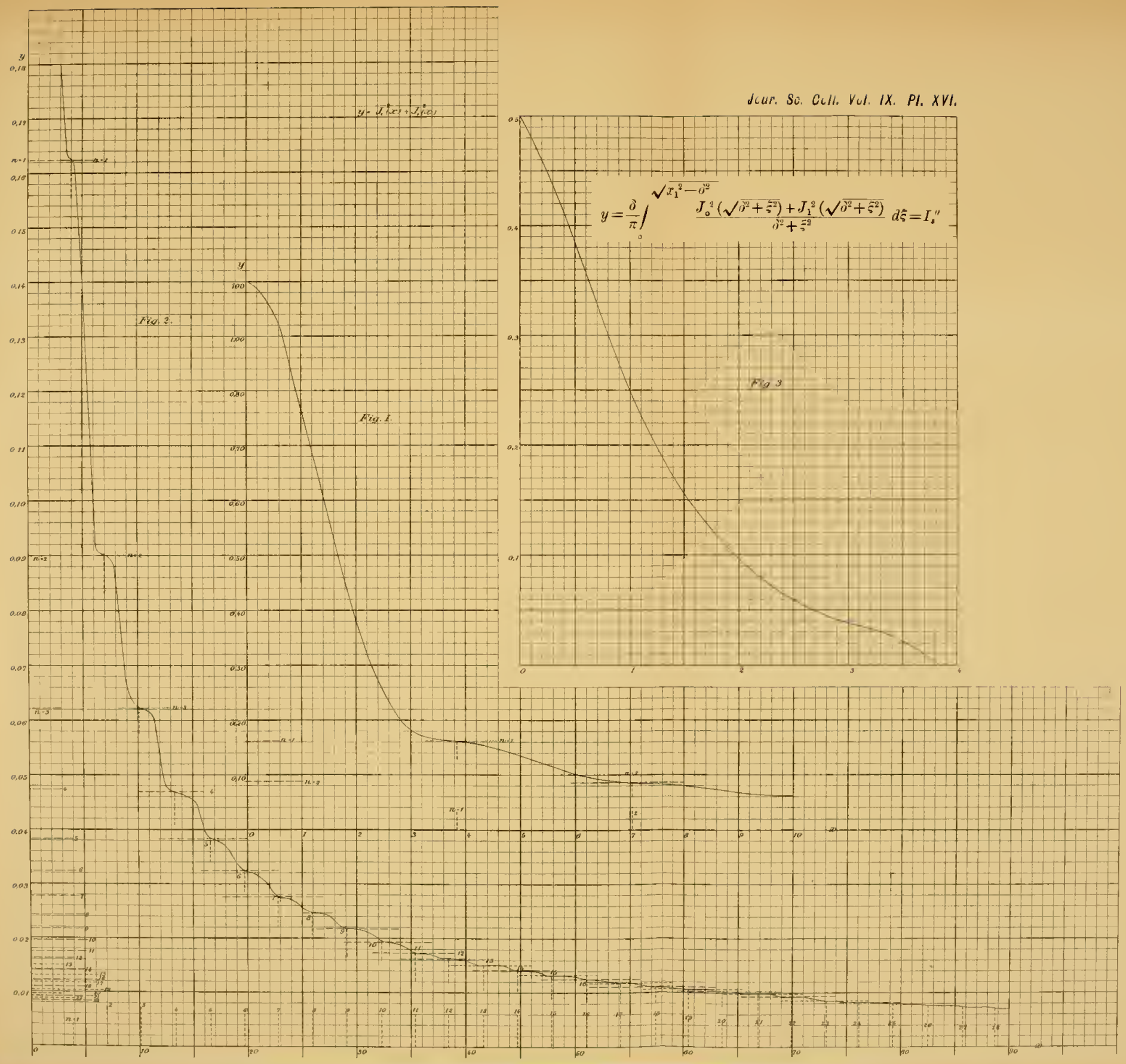
x	y	x	y	x	y
1.20	0.69871	1.60	0.53217	2.00	0.38273
1.21	0.69457	1.61	0.52812	2.01	0.37943
1.22	0.69042	2.62	0.52407	2.02	0.37613
1.23	0.68626	1.63	0.52004	2 03	0.37287
1.24	0.68210	1.64	0.51603	2.04	0.36963
1.25	0.67793	1.65	0.51201	2.05	0.36641
1.26	0.67376	1.66	0.50803	2.06	0.36322
1.27	0.66958	1.67	0.50406	2.07	0.36006
1.28	0.66539	1.68	0.50009	2.08	0.35691
1.29	0.66121	1.69	0.49614	2.09	0.35380
1.30	0.65702	1.70	0.49221	2.10	0.35071
1.31	0.65282	1.71	0.48829	2.11	0.34765
1.32	0.64862	1.72	0.48439	2.12	0.34461
1.33	0.64443	1.73	0.48049	2.13	0.34161
1.34	0.64024	1.74	0.47662	2.14	0.33862
1.35	0.63603	1.75	0.47277	2.15	0.33567
1 36	0.63183	1.76	0.46893	2.16	0.33273
1.37	0.62763	1.77	0.46510	2.17	0.32982
1 38	0.62343	1.78	0.46130	2.18	0.32694
1.39	0.61923	1.79	0.45752	2.19	0.32410
1.40	0.61502	1.80	0.45376	2.20	0.32127
1.41	0.61085	1.81	0.45001	2.21	0.31848
1.42	0.60664	1.82	0.44627	2.22	0,31571
1.43	0.60246	1.83	0.44257	2.23	0.31296
1.44	0.59827	1.84	0.43887	2.24	0.31025
1.45	0.59409	1.85	0.43521	2.25	0.30757
1.46	0.58991	1.86	0.43155	2.26	0.30491
1.47	0.58574	1.87	0.42793	2.27	0.30228
1.48	0.58158	1.88	0.42432	2.28	0.29967
1.49	0.57742	1.89	0.42073	2.29	0.29710
1.50	0.57327	1.90	0.41717	2.30	0.29454
1.51	0.56912	1.91	0.41363	2.31	0.29202
1.52	0.56497	1.92	0.41009	2.32	0.28954
1.53	0.56084	1.93	0.40660	2.33	0.28707
1.54	0.55672	1.94	0.40312	2.34	0.28463
1.55	0.55259	1.95	0.39967	2.35	0.28223
1.56	0.54849	1.96	0.39623	2.36	0.27984
1.57	0.54440	1.97	0.39283	2.37	0.27749
1.58	0.54031	1 98	0.38944	2.38	0.27516
1.59	0.53624	1.99	0.38608	2.39	0.27287

$$y = J_0^2(x) + J_1^2(x)$$

x	y	x	y	x	y
2.40	0.27060	2.80	0.20210	3.20	0.17082
2.41	0.26836	2.81	0.20091	3.21	0.17040
2.42	0.26614	2.82	0.19974	3.22	0.16999
2.43	0.26396	2.83	0.19861	3.23	0.16961
2.44	0.26181	2.84	0.19750	3.24	0.16922
2.45	0.25967	2.85	0.19640	3.25	0.16886
2.46	0.25758	2.86	0.19532	3.26	0.16851
2.47	0.25550	2.87	0.19428	3.27	0.16817
2.48	0.25345	2.88	0.19325	3.28	0.16784
2.49	0.25143	2.89	0.19224	3.29	0.16753
2.50	0.24944	2.90	0.19126	3.30	0.16723
2.51	0.24748	2.91	0.19030	3.31	0.16694
2.52	0.24555	2.92	0.18936	3.32	0.16667
2.53	0.24364	2.93	0.18844	3.33	0.16640
2.54	0.24175	2.94	0.18754	3.34	0.16614
2.55	0.23990	2.95	0.18667	3.35	0.16590
2.56	0.23808	2.96	0.18581	3.36	0.16566
2.57	0.23628	2.97	0.18497	3.37	0.16544
2.58	0.23451	2.98	0.18416	3.38	0.16523
2.59	0.23276	2.99	0.18336	3.39	0.16502
2.60	0.23104	3.00	0.18259	3.40	0.16484
2.61	0.22934	3.01	0.18183	3.41	0.16465
2.62	0.22768	3.02	0.18109	3.42	0.16448
2.63	0.22604	3.03	0.18038	3.43	0.16430
2.64	0.22443	3.04	0.17968	3.44	0.16415
2.65	0.22285	3.05	0.17899	3.45	0.16400
2.66	0.22128	3.06	0.17833	3.46	0.16386
2.67	0.21975	3.07	0.17768	3.47	0.16373
2.68	0.21825	3.08	0.17706	3.48	0.16360
2.69	0.21616	3.09	0.17645	3.49	0.16348
2.70	0.21530	3.10	0.17585	3.50	0.16337
2.71	0.21387	3.11	0.17527	3.51	0.16326
2.72	0.21246	3.12	0.17472	3.52	0.16317
2.73	0.21108	3.13	0.17418	3.53	0.16307
2.74	0.20971	3.14	0.17365	3.54	0.16299
2.75	0.20839	3.15	0.17314	3.55	0.16291
2.76	0.20709	3.16	0.17265	3.56	0.16284
2.77	0.20581	3.17	0.17217	3.57	0.16277
2.78	0.20455	3.18	0.17170	3.58	0.16271
2.79	0.20331	3.19	0.17125	3.59	0.16265

$$y = J_0^2(x) + J_1^2(x)$$

x	y	x	y	x	y
3.60	0.16260	3.70	0.16228	3.80	0.16222
3.61	0.16254	3.71	0.16227	3.81	0.16222
3.62	0.16250	3.72	0.16225	3.82	0.16222
3.63	0.16246	3.73	0.16225	3.83	0.16222
3.64	0.16243	3.74	0.16224		
3.65	0,16240	3.75	0.16223		
3.66	0.16237	3.76	0.16223		
3.67	0.16234	3.77	0.16222		
3.68	0.16232	3.78	0.16222		
3.69	0.16230	3.79	0.16222		


$y = J_1^2(x) + J_2^2(x)$
Fig. 2.
Fig. 1.
Fig. 3
$y = \frac{\delta}{\pi} \int_0^{\sqrt{x_1^2 - \delta^2}} \frac{J_0^2(\sqrt{\delta^2+\xi^2}) + J_1^2(\sqrt{\delta^2+\xi^2})}{\delta^2+\xi^2} d\xi = I_0''$

δ = 0
Fig. 8
δ = 1
Fig. 9

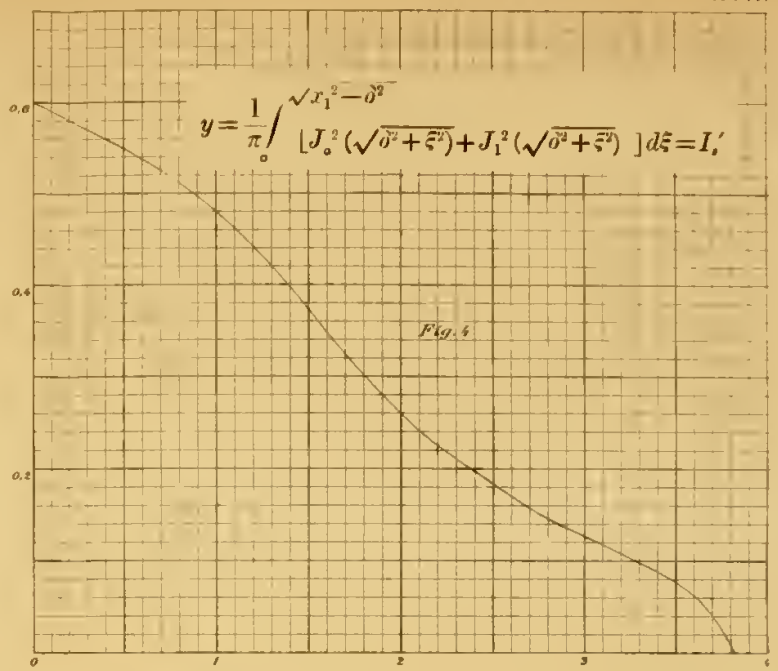

$y = \frac{1}{\pi}\int_0^{\sqrt{x_1^2-\delta^2}} [J_0^2(\sqrt{\delta^2+\xi^2}) + J_1^2(\sqrt{\delta^2+\xi^2})]\,d\xi = I_1'$
Fig. 4

Fig. 7

Fig. 6

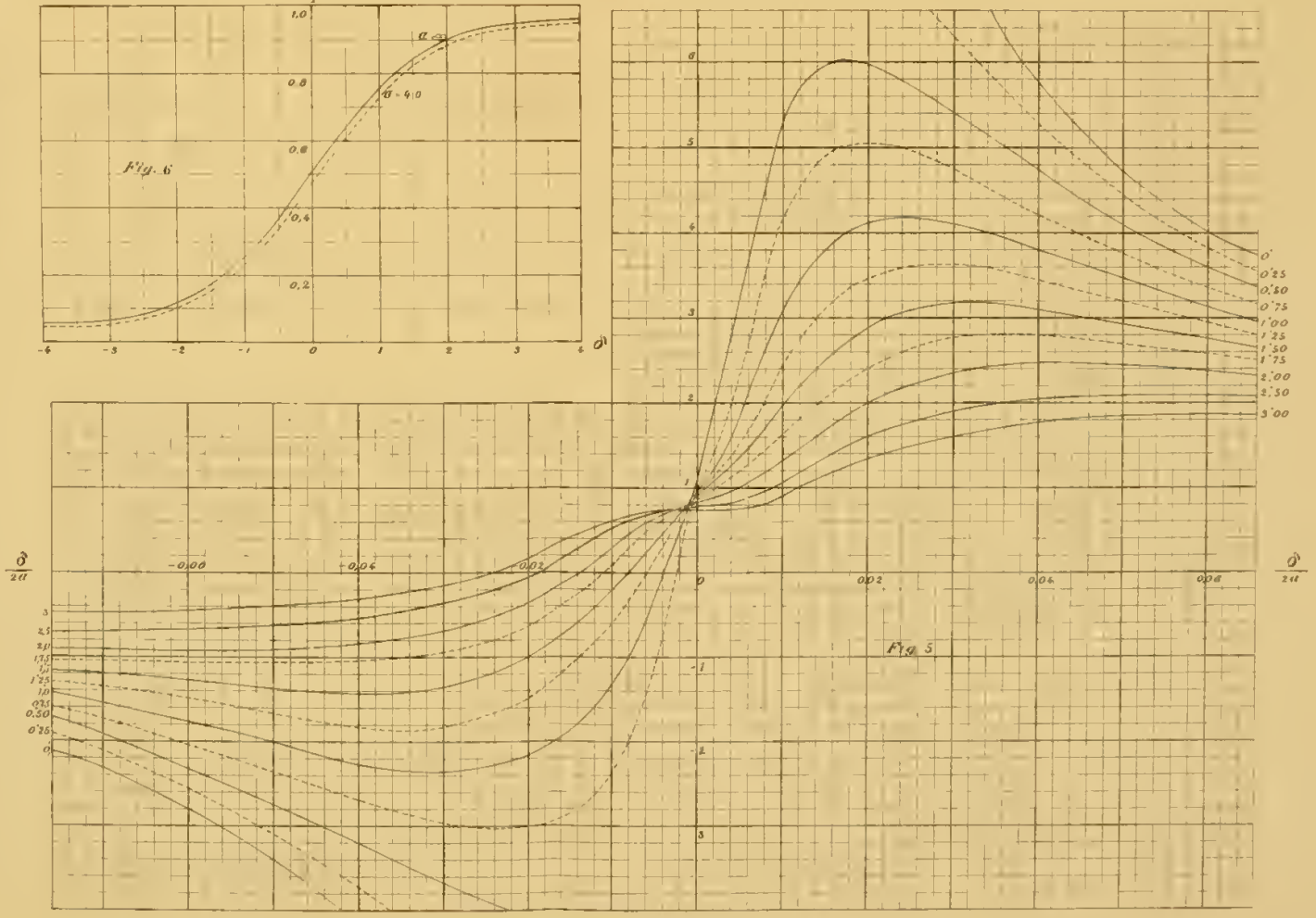


Fig. 5

Researches on Magnetostriction

By

H. Nagaoka, *Rigakuhakushi,*

Professor of Applied Mathematics,

and

K. Honda, *Rigakushi,*

Post-graduate in Physics.

With Plates XVIII & XIX.

The object of the present investigation is two-fold ; firstly, to determine the effect of hydrostatic pressure on the magnetization of iron and nickel and to find whether there exist reciprocal relations between the effects of compression and the volume change of ferromagnetics by magnetization ; secondly, to examine Kirchhoff's[1] theory of magnetostriction from the measurement of strains produced by magnetization, and from the effects of stress on the magnetization of iron and nickel.

Both experiments and theory show that physical changes are mostly reciprocal. In magnetism, the fact is markedly brought out by the mutual relation of twist and magnetization[2] as well as by the change of length by magnetization and the effect of longitudinal pull applied to the magnetized wire. The theoretical exposition of

1). Kirchhoff, *Sitzber. d. Acad. d. Wiss. zu Berlin*, p. 137, 1884 ; *Wied. Ann.* **24**, 52. 1885 ; *Gesammelte Abhandlungen, Nachtrag*, p. 91, Leipzig (1891) ; See also Pearson's *History of elasticity*, II, §§ 1313–1321.

2). See Wiedemann's *Electricität*, III (1895).

these facts was given by J. J. Thomson;[1] by applying similar reasoning to the effect of hydrostatic pressure on magnetization, we can show that the change of volume accompanying the magnetization must to some extent be reciprocal to the change of magnetization wrought out by compression.

Unfortunately our knowledge of the volume change by magnetization is so very scanty and discordant that we have had to undertake fresh experiments on the samples of ferro-magnetics used in our experiments.

The question regarding the effect of hydrostatic pressure on the magnetization is intimately connected with the thermodynamics of elastic bodies. From this standpoint, the problem was for the first time attacked by Wassmuth,[2] whose experimental results are in rough agreement with his theory. His experiments are of rather a qualitative nature, no absolute measurement of pressure as well as that of magnetization having been undertaken. H. Tomlinson,[3] in his series of experiments on the effects of stress on the properties of matter has examined this point; he concludes "Fluid pressure does not temporarily affect either the temporary magnetic susceptibility of annealed iron, or the permanent magnetization of hard steel, except, it may be, to a degree which is not comparable with that of the effect of stress in any one direction."

Although experiments on the effect of hydrostatic pressure are very scanty, the effect of one-sided pressure has been a subject of investigation by several physicists; the effect of transverse stress on the magnetization of iron was examined by Lord Kelvin,[4] and that of

1). J. J. Thomson, *Application of Dynamics to Physics and Chemistry*, chapter 4 (1888).
2). Wassmuth, *Sitzber d. Akad. d. Wissensch. zu Wien.* **86**, 2, 539, 1882.
3). H. Tomlinson, *Proc. Roy. Soc.* **42**, 230, art. 49, 1887.
4). Kelvin, *Phil. Trans.* **163**, (2), 693, 1877.

longitudinal compression by Ewing[1] and Chree.[2] Unlike all these effects, the change wrought by hydrostatic pressure is of a different order of magnitude, as remarked by Tomlinson. Without special arrangement for detecting a minute change in magnetization, we can not well measure the change produced by pressure on all sides.

In a paper on the effect of magnetic stress in magnetostriction,[3] Mr. E. T. Jones and one of us have pointed out the importance of investigating the relation of magnetization to hydrostatic pressure in deciding the intricate question of magnetostriction. Mr. Jones[4] has, however, found out that it is unnecessary to take up experiments on hydrostatic pressure, inasmuch as the quantity which is required to settle the question can be deduced by means of simple experiments on the effect of longitudinal pull on a ferromagnetic wire.

In the present investigation our attention has not been confined to the question of magnetic stress, and we have been able, after several fruitless attempts, to establish the fact that the effect of hydrostatic pressure is not immeasurably small, but that there is a remarkable reciprocal relation between the volume change by magnetization and the change of magnetization by compression.

In order to settle the question of magnetostriction, we have measured the change of length and the effect of longitudinal pull on the magnetization of iron and nickel. From the different combinations of these effects, we can calculate the coefficients k' and k'' introduced by Kirchhoff. We are thus enabled to examine the effect of stress from the strains caused by magnetization, and *vice versa*.

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1). Ewing, *Phil. Trans.* **179**, 333, 1888.
2). Chree, „ „ **181**, 329, 1890.
3). Nagaoka a. T. Jones. *Phil. Mag.* May, 1896.
4). T. Jones, *Phil. Trans.* **189**, 189, 1897.

The present paper will therefore be divided into the following sections :—

1. Change of volume produced by magnetization.
2. Change of length produced by magnetization.
3. Effect of hydrostatic and transverse pressures on the magnetization of iron and nickel.
4. Effect of longitudinal pull on the magnetization of iron and nickel.
5. Calculation of the coefficients k' and k'', and a comparison between theory and experiment.

§ 1. Change of volume produced by magnetization.

We shall hereafter consider the strain produced by magnetization as functions of the magnetizing force and the intensity of magnetization ; it will thus be necessary in the first place to determine the magnetizations of the different specimens of the ferromagnetics used in the present experiment.

The ferromagnetics examined in the present investigation had the following dimensions.

1. Ovoid of Swedish iron.

   Length of the major axis=20 cm. ; minor axis=0.986 cm. ; volume=10.18 c. c. ; mass=82 grm. ; demagnetizing factor N=0.0848.[1)]

2. Cylinder of Lowmoor iron.

   Length=25 cm. ; diameter=0.947 cm. ; volume=17.55 c.c. ; mass=136 grm. ; demagnetizing factor N=0.0533.

3. Nickel rod of square cross-section.

   Length=26 cm. ; side=0.514 cm. ; section=0.264 sq. cm. ;

1). Du Bois, *Magnetische Kreise*, Berlin und München (1894).

volume = 6.86 c. c. ; mass = 58 grm. ; demagnetizing factor N = 0.020.

The demagnetizing factor for the rod was calculated on the supposition that N was equal to that of a circular cylinder of the same cross-section.

The magnetizing coil was 30 cm. long and wound in 12 layers ; its resistance was 0.63 ohm and gave the field of 37.97 c. g. s. units at the middle of the coil due to a current of one ampère.

The magnetometer consisted of a small bell magnet suspended in a thick copper case by a quartz fibre and provided with a plane mirror. It was placed due magnetic east of the coil and its deflection was read by means of scale and telescope.

The following table gives the magnetization in different fields :—

H	Iron ovoid.	Iron cylinder.	Nickel rod.
5	700	158	47
10	1010	380	100
20	1220	770	175
30	1270	900	240
40	1300	980	280
50	1335	1027	308
75	1395	1100	358
100	1445	1143	392
125	1480	1180	414
150	1505	1210	432
200	1570	1270	455
250	1605	1315	469
300	1655	1350	377
350		1380	482

Before we proceed to describe the method employed in the present experiment, it will be worth while to compare the results

of several previous investigators on the change of volume produced by magnetization.

It was generally admitted that there is no change of volume by magnetization, but it will be easily seen that most of these experimenters tried to increase the volume of the magnet by unusually increasing the thickness instead of length, thereby incurring the risk of increasing the demagnetizing factor. They did not therefore arrive at a field strength sufficient to produce appreciable change of volume.

Joule[1] was the first to call attention to the change of volume which may accompany the magnetization of iron. The result was in the negative, but as he did not give the strength of the magnetizing current or the intensity of magnetization, it is difficult to compare his result with that of his successors. It is beyond doubt that the change of volume was very minute, and there was sufficient evidence that the elongation in the direction of magnetization is accompanied by contraction in the direction perpendicular to it.

The elaborate researches of Cantone[2] on the strain of a ferromagnetic ovoid are not free from the fault above mentioned. The length of the major axis of the ovoid was 16.7 times that of the minor, so that the demagnetizing factor = 0.1134. As his results are given in terms of the magnetizing current and the moment of the magnet, we have thought it advisable to recalculate the result in H ($=H_0-N\,I$ where H_0 stands for the magnetizing field in the coil) and I (in C.G.S. units).

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1). Joule, *Phil. Mag.* **30**, 76, 1847, *Collected Works* **I**.

2). Cantone, *Memoria d. Accad. d. Lincei* **6**, 1890; *Rendiconti d. Accad. d. Lincei* **6**, (1), 257, 1890.

The following table gives Cantone's determination of the intensity of magnetization :—

H_0	H	I
13.5	2.0	102
26.7	3.8	202
38.1	4.4	293
51.6	6.8	397
58.5	7.5	450

It will be seen from the above table that on account of the great demagnetizing factor, the magnetizing force was less than 8 C.G.S. units, although the field in the coil was nearly 60.

Cantone did not observe any alteration of volume in the iron ovoid even with a magnetizing current of 12 ampères ; but it is quite probable that the intensity of the magnetizing force as well as that of magnetization was insufficient to produce appreciable change.

On account of the small susceptibility of nickel, the effect of the demagnetizing factor in Cantone's nickel ovoid was not so marked as in the iron ovoid. So far as we are aware, he was the first to notice the diminution of volume in nickel by magnetization. Although his measurements with dilatometer filled with water and with alcohol are widely discordant, it is beyond doubt that the readings with alcohol are the more reliable for reasons which will be afterwards given. His calculation of Kirchhoff's coefficients k' and k'' based on the measurement of the change of length and of volume in nickel by magnetization throw much light on the theory of magnetostriction.

Our knowledge of the change of *internal* capacity of tubes of iron, steel, and nickel in the magnetic field has been largely ex-

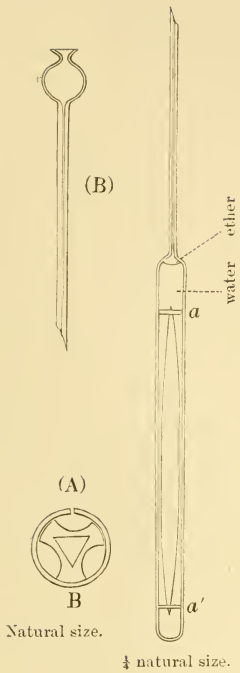
tended by the numerous researches of Dr. C. G. Knott.[1] It is much to be regretted that the magnetization was not uniform in his experiments, and that consequently the change of volume could not be expressed as a function of the magnetization. If the field within the magnetized body be not uniform, then there will be internal forces A, B, C, according to Kirchhoff, and the discussion will thereby be rendered very tedious. As the length of the magnetizing coil is not given in Dr. Knott's experiments, it is rather difficult to estimate the mean field strength ; but as the length of the magnet was about 46 cm., while the field strength at the distance of 21.9 cm. from the centre of the coil was 0.937 from that at the middle, it would appear that the field at the ends of the magnet was widely different from the mean value. The discussion of the result is rendered doubly difficult by the influence of the steel or brass cap for fixing the capillary tube to the hollow cylinder. Such inconvenience will disappear if the change of volume of the magnet itself be observed, as is easily possible, if sufficient precautions be taken in the arrangement of the measuring apparatus.

These circumstances show that the question regarding the change of volume by magnetization is by no means settled ; and as almost all theories of magnetostriction make the strain in ferromagnetics depend on the intensity of magnetization and that of the magnetizing force, we have examined the alteration of the volume as functions of these two quantities.

The change of volume was determined by means of a dilatometer. The specimen to be tested was placed in a glass tube provided with a capillary neck (Fig. 1.). The upper part of the

1). Knott, *Transactions of Roy. Soc., Edinburgh*, **38**, 527, 1896.

Fig. 1.



capillary tube (section) with reservoir for filling the dilatometer with liquid is shown in (B). In supporting the ovoid in the tube, care was taken not to let it touch the sealed end of the glass tube. Two circular brass rings (a) (a') were inserted in the tube, and made to fit tightly against the wall of the glass. A brass plate of the form given in (A) was soldered to the ring at a. The ends of the ovoid were then placed loosely within the triangular holes. The ovoid was thus supported in the central line of the dilatometer without touching the walls of the tube. A similar arrangement was employed for supporting the nickel rod within the dilatometer.

To prevent the rusting of the iron, the dilatometer was filled with a very dilute solution of caustic soda nearly up to the neck. The capillary tube and a small portion of the main tube near the neck contained ether. When the dilatometer was all filled with water or with petroleum, the indication of the volume change was very irregular, as the fine drops of the liquid stuck to the wall of the capillary tube and the liquid was not sufficiently mobile. Cantone[1] observed the same thing when measuring the change of volume of a nickel ovoid. It would have been easier to fill the dilatometer all with ether, but there was a difficulty then in observing, owing to the great expansion

1). Cantone, *loc. cit.*

of the liquid due to the heating of the coil. We consider that the present mode of filling a dilatometer provided with fine capillary tube can be successfully applied in other cases of a similar nature.

The ovoid was placed in the middle of the magnetizing coil and the rise or fall of the meniscus in the capillary tube was observed by means of a microscope with micrometer ocular. Although the resistance of the coil was only 0.6 ohm, the heating effect was considerable, so that only an instantaneous observation could be made. This difficulty was to a great extent overcome by passing the current for some time in the coil; the ovoid was then demagnetized by the method of reversals; waiting for a time, the meniscus became stationary, the magnetizing current was then made and the reading taken. The measurement was made in a dark room, with gas-light with ground glass shade at some distance behind the capillary tube; by this arrangement, the meniscus was sharply defined.

The following table gives the determination of the change of volume in the iron ovoid and cylinder by magnetization.

Ovoid.

H	I	$\frac{\partial v}{v}$
2	155	0.1×10^{-7}
3	340	0.3
4	540	0.3
6	800	0.6
12	1105	0.9
17	1200	1.1
29	1270	1.3
49	1335	1.6
113	1470	1.7
151	1510	1.8
203	1560	1.9
251	1630	2.1

Cylinder.

H	I	$\frac{\partial v}{v}$
5	186	0.1×10^{-7}
8	308	0.2
14	598	0.3
23	804	0.5
34	912	0.6
51	1000	0.8
85	1110	0.9
102	1140	1.0
155	1220	1.2
207	1280	1.3

These numbers plotted against H, I, and I^2 are shown in Figures 1, 2, 3 (Pl. XVIII). Fig. 1 shows that the volume of iron increases very rapidly at first with the magnetizing force, but it soon reaches the 'Wendepunkt,' and then increases asymptotically with further increase of the field strength. Fig. 2 shows that the increase of volume takes place very slowly with the increase of magnetization, but goes on very rapidly as the magnetization becomes stronger. It will be seen from Fig. 3 that the increase of volume is approximately proportional to the square of the intensity of magnetization.

Bidwell found, from the measurement of the change of dimension of iron rings, that there is a diminution of volume in low field, and experiments by Dr. Knott on the change of internal volume seem to confirm this. In the present experiments with ovoid or cylinder, we found no such diminution, but always increase of volume in iron. Excepting in low fields, the change of volume is in rough agreement with that of the tube of wide bore used in Dr. Knott's experiments.

The following table gives the determination of the change of volume in the nickel rod.

H	I	$\frac{\delta v}{v}$
55	320	-0.6×10^{-7}
74	360	-0.8
101	396	-1.2
127	416	-1.4
152	432	-1.9
188	450	-2.2
288	476	-2.7
391	484	-3.1
640	490	-3.4

Nickel always shows diminution of volume, and the change is greater than in iron. From Figs. 4, 5, 6, we gather the following facts: in low fields the diminution of volume is at first very slow, and then rapid, until it reaches the 'Wendepunkt,' where it becomes steady though slower.

As determined by *external* measurements, the diminution of the volume of nickel with feeble magnetization is very slight, but it becomes very rapidly greater as the magnetization is made stronger, so that the change is nearly proportional to the square of the magnetic intensity. This is contrary to what Dr. Knott found as regards the initial behaviour of nickel which, according to him, increases in volume in low fields, and although our observations in high fields agree with his as to the quality of the change, they yet indicate the change in volume to be nearly ten times less than he made it out to be. It is to be noted however, that whereas our measurements of the volumes have been *external*, his were made on the changes in the *internal* capacity of a nickel tube.

§ 2. Change of length by magnetization.

It would be superfluous to give minute details of the measurement of the change of length by magnetization. The apparatus was the same as that used by one of us[1] some years ago in the investigation of the effects of hysteresis on the change of length. It consisted of a simple optical lever with an arrangement for temperature compensation on the same principle as the grid-iron pendulum. The mirror described in the former paper was, this time, replaced by a small total reflecting prism.

The measurements of the change of length in iron and nickel are given in the following table with corresponding values of H and I.

1). Nagaoka, *Phil. Mag.* **37.** 131, (1894); *Wied. Ann.* **53.** 487, (1894).

Iron ovoid

H	I	$\frac{\delta l}{l}$
3.0	350	1.1×10^{-7}
4.2	540	5.8
5.8	970	11.3
8.1	920	22.7
14.2	1160	28.3
29.8	1270	33.1
50.9	1340	31.6
85.6	1420	28.0
112.9	1467	23.8
150.5	1505	16.6
210.0	1565	8.3
253.1	1610	2.5
306.0	1660	−6.4

Nickel rod

H	I	$\frac{\delta l}{l}$
15	143	$-\ 11.3 \times 10^{-7}$
53	315	− 69.4
74	355	− 95.3
98	394	−124.0
122	414	−142.6
177	444	−172.8
255	474	−190.8
337	483	−207.0
507	485	−216.5

These changes are plotted against H and I in Figs. 7, 8 (Pl. XVIII). It will be seen from these curves that the change of length produced in the ovoid or in the nickel rod is similar to that observed by one of us and described in the papers above cited.

The determinations are in close agreement with the results of Bidwell and several other investigators. Inspection of these curves for nickel reveals a striking resemblance to similar curves for the change of volume in the same metal. The behaviour of iron is entirely different both as regards change of volume and change of length.

§ 3. Effect of hydrostatic and transverse pressure on the magnetization of iron and nickel.

The remarkable effect produced by longitudinal pull or compression on the magnetization of ferromagnetics promised the outcome

of a similar result by the application of hydrostatic pressure, as in the experiments of Wassumth.[1] No such marked influence of compression was however observed, but a feeble change in the reading of the magnetometer showed that the effect was not immeasurably small. It was only by special arrangement that the nature of the change could be clearly made out.

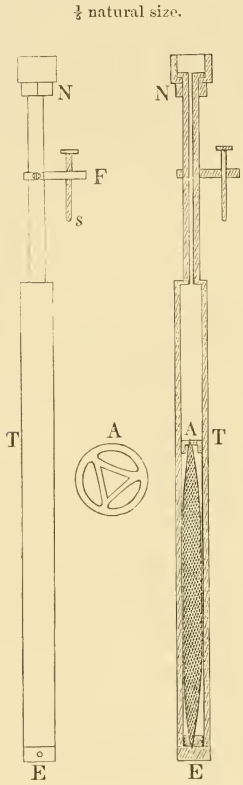


Fig. 2.

The hydrostatic pressure was given by means of Cailletet's pump for liquefying gases. The pump was provided with Ducretet manometer indicating pressures up to 300 atmospheres. These indications on being gauged by measuring the volume of dry air gave wide differences from the actual pressure, the relation between volume and pressure being taken from Natterer and Amagat's results. One end of a seamless copper tube (length 4.7 m., internal diameter 3 mm., and external diameter 7 mm.) was attached to the pump; by pumping in water into the tube, pressure was communicated to a vessel containing the iron or nickel which is to be compresssed.

The ovoid or rod, which was to be examined under different pressures, was enclosed in a stout brass tube T (internal diameter 1.1 cm., external diameter 2.0 cm., length 31 cm.) filled with water. The tube fitted loosely in the magnetizing

1). Wassumth, *loc. cit.*

coil. The lower end of the ovoid was placed in a conical hole, bored in the end screw E fitting into the main tube T. To prevent dislocation of the ovoid and to keep it always vertical, the upper end was loosely fitted into a triangular hole in the brass plate A in the manner already described in the determination of the change of volume. The neck of the vessel consisted of a smaller brass tube provided with a flange F ; by means of a strong brass screw S attached to F, the whole vessel can be slowly moved in the solenoid, so that there was no difficulty in placing the magnetized body in proper position for experiment.

The vessel was connected with the copper tube from the pump by a screw nut N. Before an experiment, it was always necessary to apply the pressure of more than 250 atmospheres to test if there was no leakage at the screw joints.

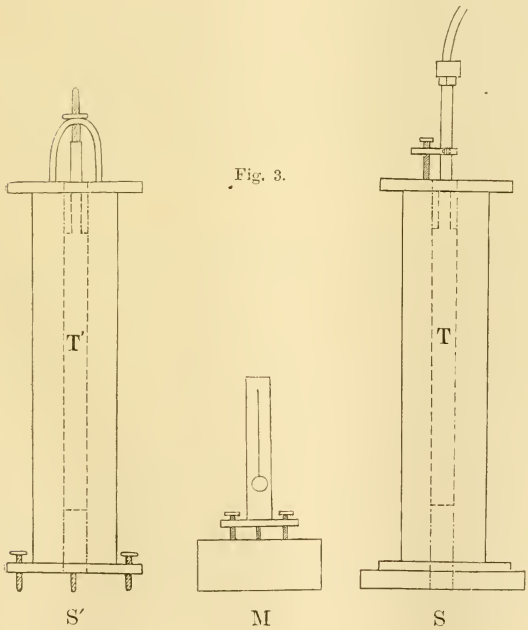


Fig. 3.

Two such brass tubes, T and T′, each containing a magnet of the same geometrical form and size, were placed in the solenoids, S and S′ (Fig. 3), which also were of equal dimensions, as shown in

the accompanying figure. The coils were each 40 cm. long, wound in 6 layers and gave the field of 17.7 C. G. S. units for a current of one ampere. The magnetometer M was placed midway between the solenoids, due magnetic east and west. When the current was made, the magnetization of two similar bodies produced nearly the same effect on the magnetometer in the opposite sense ; thus, the deflection of the magnetometer was so compensated that the magnetometer could be placed very near the solenoids, and thereby rendered sensible to a slight change in the condition of the magnetized body. In order to make the compensation exact, the auxiliary solenoid, S′, was provided with levelling screws and the brass tube containing an auxiliary magnet with screw for adjusting the vertical position of the magnet. The magnetizing solenoid was firmly fixed to the solid stone pier, so that there was no risk of its being disturbed by the application of pressure to the vessel through the bent copper tube ; it was also ascertained by means of a long thread pendulum attached to the solenoid that no appreciable displacement of the solenoid took place during the application or removal of pressure.

To make the reading of the magnetometer sensitive, it was necessary to place the magnet in a position suitable for maximum deflection ; this could be effected either by calculation for the ovoid[1] or be experimentally determined for other shapes. The brass vessel was moved slowly up and down to such a position that it was not affected by the small vertical displacement, thus giving the position of maximum deflection. It was necessary to place the magnet in the above position, owing to a slight displacement, due to the strain caused by the strong pressure. For a vertical strain component, the magnetometer could remain practically unaffected in the position above chosen.

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1). Nagaoka, *Wied. Ann.* **57**, 275, (1896).

It will be clear from the arrangement for compensation that not only was the effect of magnetization on the magnetometer to a great extent compensated, but the effect of rise of temperature due to the magnetizing current was also provided for, since the auxiliary magnet was enclosed in a similar brass tube and placed in the coil of the same dimension and resistance. It is to be remarked that the compensation was never exact, for although the ovoids or the rods were made of the same material, there was some difference of quality as regards magnetization. Thus the compensation, though exact in certain fields, was not fulfilled throughout the whole range of fields ; nevertheless, the difference was not very great, and we believe that the influence of the rise of temperature or that of strain due to pressure will not have been so large as to materially deteriorate the experimental results. In spite of this, care was taken to keep the field during the experiment constant by watching the indication of the deci-ampere balance, by which the current was measured ; further, it was generally possible to perfect the compensation for feeble change of current by slightly shifting the auxiliary magnet or the coil.

The horizontal component of the terrestrial magnetic force was slightly affected by thus placing the coils very near the magnetometer, and it became necessary to measure the period of vibration of the magnetometer magnet by means of a chronograph, and to apply the correction to the measured intensity of magnetization.

The change in the intensity of magnetization due to the alteration of volume is evidently nearly equal to $-I\frac{\delta v}{v}$. The diminution of volume will therefore produce increase of magnetization. It will be seen that the correction due to the contraction of volume of the magnet is of the same order as the change in magnetization wrought by compression, from which the smallness of the effect can be easily judged.

Results in iron :—A few of the observed results with the iron ovoid or cylinder are given in Figs. 9 and 10 (Pl. XIX). The dotted lines indicate the correction due to the change of volume by compression, which must be added to the apparent change. These figures show that there is only minute diminution of magnetization by the application of hydrostatic pressure ; in fact, the apparent change measured in C.G.S. units does not even amount to 0.1 with a pressure of 250 atmospheres. At the above mentioned pressure, the change for H=54 is less than $\frac{1}{20000}$ of the intensity of magnetization. During a pressure cycle, there is distinct hysteresis, and the curve of the change of magnetization generally forms a single loop. On account of the inconstancy of the field, the measurement with the ovoid could not extend beyond H=15 ; with the iron cylinder, H=54 was the strongest field, in which the cyclic change could safely be observed.

If from experiments of pressure cycles, the curves for constant pressure in different fields be plotted, we obtain Figs. 11 and 12 (Pl. XIX), when the change of magnetization due to the contraction of volume is not taken into account ; if the correction be applied, then we obtain Figs. 13 and 14. These curves show that the range of the change in magnetization due to pressure increases with the field ; the increase takes place very rapidly at first, but becomes asymptotic in a moderate field. Plotting these changes against magnetization we obtain Fig. 15 which indicates that the change is nearly proportional to the intensity of magnetization.

Comparing these curves with those for the change of volume by magnetization, we find similarity between the two. It is interesting to note that whereas increase of magnetization produces increase of volume in iron, diminution of volume produces diminution of magnetization. Thus a reciprocal relation between the strain

caused by magnetization and the effect of compressional stress on magnetization is established.

Results in nickel :—The curves of a pressure cycle are shown in Figs. 15 and 16. The change of magnetization due to hydrostatic pressure is also very small, but is comparatively greater than that in iron and the hysteresis during the cycle is more decided. Whereas hydrostatic pressure causes the diminution of magnetization in iron, it causes increase of magnetization in nickel. Like other effects of stress such as stretching or twisting, we find that the change in iron is opposite to that in nickel.

The curves of the change of magnetization by constant pressure (Figs. 17, 18, 19, 20) (Pl. XIX) in different fields show that there is increase of magnetization in weak fields until it reaches a maximum in moderate fields ; it then goes on slowly decreasing. This feature is characteristic of all pressures up to 250 atmospheres. Plotted against magnetization, the general appearance of the curves is the same as that for magnetizing fields.

Comparing these curves with those obtained from change of volume by magnetization, we notice that whereas increase of magnetization produces diminution of volume in nickel, diminution of volume produces increase of magnetization.

It will be shown later on that the minuteness of the effect of compression on the magnetization of iron and nickel leads to an important conclusion in the theory of magnetostriction.

Effect of transverse stress on the magnetization of an iron tube :—Lord Kelvin,[1] in his series of experiments on the electrodynamic quality of metals, investigated the effect of transverse stress on the magnetization of an iron tube, by subjecting the inner surface of a gun barrel to

1) Kelvin, *loc. cit.*

hydrostatic pressure. In our experiment, it was of no small importance to try similar experiments with iron, in order to decide whether the minute change produced by all-sided pressure was also characteristic of the effect of transverse stress produced by pressure on the external surface of an iron or nickel tube.

To the extremities of a hollow iron cylinder (external diameter 0.47 cm., internal diameter 0.20 cm.) were soldered two thick brass caps as shown in Fig 4., and placed in the compressing vessel above described. By pumping in water to the vessel, the iron tube was subjected to pressure on its lateral surface alone, and the change of magnetization tested in the manner above described. It was soon noticed that the effect was enormously large and opposite to that of all-sided pressure. By keeping the pressure constant, the difference in the magnetization, when the tube was in the strained and unstrained state, was determined for different fields; the curves of the change in magnetization thus obtained for pressures of 50, 150 and 250 atmospheric pressures are shown in Fig 21.

Fig. 4

The present experiment is just the reverse of Lord Kelvin's,[1] and the inspection of the figures will show that the result is also just the reverse. With increase of the magnetizing force, there is increase of magnetization till it reaches a maximum, thence to diminish in stronger fields. As the field is increased, the decrease of magnetization after once reaching a critical value is so great that the magnetization in strong field is less than in the unstrained condition.

The result is thus in close agreement with Lord Kelvin's anticipation that the effects of positive pressure will be opposite to the effects

1). Kelvin, *Phil. Trans.* **152** p. 64, 1878; *Mathematical* and *Physical Papers*, II. p. 370, 1884.

of negative pressure. It is to be remarked that a solid cylinder of iron with the brass cap as shown in the above figure does not show appreciable change of magnetization with the utmost pressure available in the present experiment.

The experiments indicate that the application of stress so as to produce no shear affects the magnetization of iron or nickel only very slightly, but the remarkable change in magnetization, produced by tensional or compressional stress applied longitudinally, as well as that due to twisting wrench, is always accompanied by the shearing strain—a result, which will be of no small value in the theory of molecular magnetism.

§ 4. Effect of longitudinal pull on the magnetization of iron and nickel.

The above subject has been investigated by several experimenters, but so far as we are aware, the change in the magnetization of iron and nickel by the application of feeble stress is scarcely known. It will be seen from the experiments on the strains produced by magnetization that the strain corresponds to the effect of a very feeble stress. As our principal object in the present investigation was a comparison of Kirchhoff's theory of magnetostriction with the experimental results, we found it necessary to pay special attention to the change in the magnetic qualities of iron and nickel, when these ferromagnetics are subjected to small longitudinal pull, which will strain these metals to a degree comparable with the deformation in the magnetizing field.

As the iron ovoid used in the preceding experiment was unfit for studying the effect of the longitudinal pull, an iron rod of 0.27 sq. cm. section made of the same material as the ovoid was used for measuring the change of magnetization in the free and in the feebly

stretched condition. The nickel rod used in all the preceding experiments was also examined. The magnetometer was made sensitive by means of the compensation arrangement, used in the measurement of the effects of hydrostatic pressure. The difference in the magnetization of the rod to be examined and that of the auxiliary rod was first examined in the unstrained state; then loading the rod, the difference in the magnetization was again determined; the difference of these two determinations was evidently the effect sought.

The following table gives the change of magnetization in different fields due to longitudinal stresses (0.19 kg. sq. mm.) and (0.38 kg. sq. mm.).

Iron

H	δ I (0.19 kg.sq.mm.)	δ I (0.38 kg.sq.mm.)
6.1	+ 1.01	+ 2.15
9.6	+ 2.95	+ 5.46
15.5	+ 3.10	+ 5.74
20.4	+ 1.85	+ 3.72
27.3	+ 0.64	+ 2.00
34.6	− 0.13	+ 0.92
42.5	− 0.56	+ 0.24
50.8	− 0.77	− 0.11
67.6	− 0.86	− 0.49
84.6	− 0.94	− 0.69

Nickel

H	δ I 0.19 kg sq. mm.)	δ I (0.38 kg.sq.mm.)
7.9	+ 0.52	+ 0.63
14.5	− 4.62	− 6.96
22.2	− 5.34	− 8.35
30.2	− 4.82	− 8.13
38.5	− 4.16	− 7.07
47.1	− 3.73	− 5.85
55.3	− 3.45	− 5.02
63.9	− 3.21	− 4.41
81.0	− 2.77	− 3.27
98.3	− 2.44	− 2.44

The magnetization of iron in the stretched state increases with the magnetizing force till it reaches a maximum in H=13 C.G.S. nearly; it then goes on slowly diminishing till it becomes less than in the free state.

In nickel there is generally decrease of magnetization in the stretched state, except in weak field, where a slight increase of magnetization was observed. Corresponding to the critical field in iron, for which the change of magnetization is a maximum, there exists also a critical field in nickel for which the diminution of magnetization is a maximum. Further, it will be seen from the figures that the change of magnetization is not exactly proportional to the amount of longitudinal stress.

Denoting the longitudinal stress by P, the ratio $\frac{\partial I}{\partial P}$ gradually decreases with increased loading; in nickel the ratio $\frac{\partial I}{\partial P}$ diminishes at a greater rate as the field is increased. The rate of diminution seems apparently to be smaller in a rod with smaller loading.

It appears from Prof. Ewing's[1] experiment that the increase of magnetization in iron in weak field becomes more pronounced with greater loading, but the field at which the magnetization becomes smaller than in the unloaded state recedes towards the weaker side. Although Prof. Ewing did not observe these points in fields greater than H=8 for 2 kg. loading, which is far greater than that in the present experiment, the general feature of the curves of magnetization shows that if the loading be greatly diminished, the above-mentioned field will become correspondingly large. Thus the present investigation agrees in its general features with Prof. Ewing's experiments.

In nickel, a slight increase of magnetization in weak field was observed with the stretched rod; whether this has any connection with the Villari effect observed by Heydweiller[2] is a question, which without special examination can not be easily decided.

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1). Ewing, *Phil. Trans.* **196** (2) 607, 1885.
2). Heydweiller, *Wied. Ann.* **52**, 442, 1894.

§ 5. Calculation of Kirchhoff's coefficients k and k . Comparison between theory and experiment.

According to Kirchhoff's theory of magnetostriction,[1] the coefficients k, k', k'' are defined by the equations

$$I_x = \left\{ k - k' \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) - k'' \frac{\partial u}{\partial x} \right\} H_x ,$$

$$I_y = \left\{ k - k' \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) - k'' \frac{\partial v}{\partial y} \right\} H_y ,$$

$$I_z = \left\{ k - k' \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) - k'' \frac{\partial w}{\partial z} \right\} H_z ,$$

where I_x, I_y, I_z are the components of the intensity of magnetization I, H_x, H_y, H_z the components of the magnetizing force H, u, v, w the component displacements of the medium at point $x\ y\ z$. The coefficient k is nearly equal to susceptibility as the strains due to magnetization is negligibly small. The determination of the coefficients k' and k'' involves considerable difficulty, because the strains produced by magnetization or the effect of stress on magnetization generally depend on both of these coefficients.

In a joint paper with Mr. E. T. Jones, one of us remarked that the easiest method of testing Kirchhoff's theory would be to measure the change of volume of a ferromagnetic ring. The volume change would be theoretically equal to $\frac{\delta v}{v} = 3\frac{\delta l}{l} = \frac{3\ H}{4K(1+3\theta)}(I - k'H)$. Unfortunately there is great experimental difficulty, if the test be made by means of a dilatometer, except in the manner introduced by Bidwell[2] of measuring the change in the section of the ring.

Cantone[3] found that the change of length and of volume of an elongated ovoid are given by the formulæ

1). Kirchhoff, *loc. cet*; see also Pockels, *Archiv f. Mathem. u. Physik* (2) **12**, 1893.

2). Bidwell, *Proc. Roy. Soc.* **56**, 94, 1894.

3). Cantone, *loc. cit.*

$$\frac{\delta l}{l}=\left\{\frac{4\pi k^2}{3}\left(\frac{1+\theta}{1+2\theta}\right)+\left(\frac{k-k'}{2(1+2\theta)}\right)-\frac{k''}{2}\right\}\frac{H^2}{E}, \qquad (a)$$

$$\frac{\delta v}{v}=\frac{H^2}{K(1+3\theta)}\left\{\pi k^2+\frac{3(k-k')}{4}-\frac{k''}{4}\right\}, \qquad (b)$$

where E is Young's modulus and K the rigidity, θ being a constant defined by the equation

$$\frac{E}{2}\left(\frac{1+2\theta}{1+3\theta}\right)=K.$$

In the above formulæ, the terms involving the ratio $\left(\frac{\text{minor axis}}{\text{major axis}}\right)^2$ are not taken into account.

Corresponding expressions for a long prismatic body placed in a uniform magnetic field can be approximately calculated in the following manner.

Let the field strength in the coil be denoted by H_0; then the potential of the resultant magnetizing force would be

$$\varphi=-\frac{H_0}{1+Nk}\cdot x$$

where N is the demagnetizing factor, k the susceptibility and x the direction of magnetization. Thus

$$\varphi=-Hx.$$

Supposing that the magnetization is uniform, the component of the internal force would be (using Kirchhoff's notation)

$$A=\frac{1}{2}\left(k'+\frac{k''}{2}\right)\frac{\partial H^2}{\partial x}=0,$$

$$B=0, \qquad C=0.$$

The surface traction on the end-faces, which we consider to be perpendicular to x axis, has components

$$\overline{A}_1=H^2\left(2\pi k^2+\frac{k-k'-k''}{2}\right)=aH^2$$

$$\overline{B_1}=0, \qquad \overline{C_1}=0.$$

On the lateral faces,

$$\overline{A_2}=0,$$

$$\overline{B_2}=\frac{k-k'}{2}H^2 \cos\theta=\beta H^2 \cos\theta,$$

$$\overline{C_2}=\frac{k-k'}{2}H^2 \cos\theta=\beta H^2 \cos\theta,$$

where θ is the angle made by the normal with y axis. Thus the surface traction

$$\overline{X_n}=\alpha H^2=-X_x,$$

$$\overline{Y_n}=\beta H^2 \cos\theta=-Y_y \cos\theta,$$

$$\overline{Z_n}=\beta H^2 \sin\theta=-Z_z \sin\theta,$$

and $Y_z=Z_x=X_y=0$, which satisfies the equations

$$\frac{\partial X_x}{\partial x}+\frac{\partial X_y}{\partial y}+\frac{\partial X_z}{\partial z}=0,$$

$$\frac{\partial Y_x}{\partial x}+\frac{\partial Y_y}{\partial y}+\frac{\partial Y_z}{\partial z}=0,$$

$$\frac{\partial Z_x}{\partial x}+\frac{\partial Z_y}{\partial y}+\frac{\partial Z_z}{\partial z}=0.$$

Thus we get the equations

$$-X_x=2K\left(\frac{\partial u}{\partial x}+\theta\sigma\right)=\alpha H^2,$$

$$-Y_y=2K\left(\frac{\partial v}{\partial y}+\theta\sigma\right)=\beta H^2,$$

$$-Z_z=2K\left(\frac{\partial w}{\partial z}+\theta\sigma\right)=\beta H^2,$$

where $$\sigma=\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}+\frac{\partial w}{\partial z}.$$

These equations give

$$\sigma = \frac{(\alpha+2\beta)}{2K(1+3\theta)} H^2 = \frac{\gamma}{2K\theta} H^2,$$

or $$\sigma = \frac{\delta v}{v} = \frac{H^2}{2K(1+3\theta)} \left\{ 2\pi k^2 + \frac{3}{2}(k-k') - \frac{k''}{2} \right\}. \qquad (c)$$

Similarly we obtain

$$u = \frac{\alpha-\gamma}{2K} H^2 x \quad ,$$

$$v = \frac{\beta-\gamma}{2K} H^2 y \quad ,$$

$$w = \frac{\beta-\gamma}{2K} H^2 z \quad .$$

The elongation in the direction of magnetization is

$$\lambda = \frac{\delta l}{l} = \frac{H^2}{E} \left\{ 2\pi k^2 - \frac{k''}{2} + \frac{(k-k')}{2(1+2\theta)} \right\}. \qquad (d)$$

Supposing that the Poisson ratio is $\frac{1}{4}$, or $\theta = \frac{1}{2}$, we find for a prismatic body

$$\lambda = \frac{\delta l}{l} = \frac{I^2}{E} \left(2\pi + \frac{k-k'}{4k^2} - \frac{k''}{4k^2} \right),$$

$$\sigma = \frac{\delta v}{v} = \frac{I^2}{E} \left(\pi + \frac{3(k-k')}{4k^2} - \frac{k''}{4k^2} \right).$$

Corresponding formulæ for the ovoid are, according to Cantone,

$$\lambda = \frac{\delta l}{l} = \frac{I^2}{E} \left(\pi + \frac{k-k'}{4k^2} - \frac{k''}{2k^2} \right) \quad ,$$

$$\sigma = \frac{\delta v}{v} = \frac{I^2}{E} \left(\pi + \frac{3(k-k')}{4k^2} - \frac{k''}{4k^2} \right) .$$

Comparing the formulæ (*a*) (*b*) (*c*) (*d*), we find that the change of volume is the same for the ovoid as for the prismatic body; the difference in the length change is equal to $\frac{2(1+4\theta)I^2}{3(1+2\theta)E}$, being slightly greater for the prismatic body than for the ovoid.

The formulæ (*c*) (*d*) are never exact, as prismatic bodies can not be magnetized uniformly, and consequently there must be also internal forces acting. But to the first approximation we can use these formulæ, inasmuch as the strain caused by magnetization can only be roughly measured. Mr. Jones[1] employed (*a*) for a nickel wire; the difference $\pi\frac{I^2}{E}$ is, however, very small in nickel, so that there will be no great discrepancy in the final result.

The change in magnetization due to increase of volume σ by hydrostatic pressure is evidently

$$\delta I = -H\left(k' + \frac{1}{3}k''\right)\sigma, \qquad (e)$$

and the change of susceptibility due to longitudinal stretching λ of a prismatic body

$$\delta k = \left\{ k'\frac{E}{K} - 3\left(k' + \frac{1}{3}k''\right)\right\}\lambda. \qquad (f)$$

For the determination of the coefficients k' and k'', the combination of the experimental data in any two sets of the experiment already described can be conveniently used. In order to test Kirchhoff's theory, we have calculated k' and k'' from experiments on the change of volume and of length by magnetization, and compared them with values deduced from experiments on the change of magnetization produced by compression and by stretching. Thus, for a prismatic body, we obtain from (*c*) and (*d*)

$$\text{(A)} \qquad \begin{cases} k' = k + \dfrac{E^2}{2KH^2}\Big(\lambda - (1+2\theta)\sigma\Big), \\[2ex] k'' = 4\pi k^2 - \dfrac{E^2}{2KH^2}\Big(3\lambda - \sigma\Big); \end{cases}$$

for an ovoid, we obtain from (*a*) and (*b*)

1). E. T. Jones, *loc. cit.*

$$\text{(B)} \qquad \begin{cases} k' = \dfrac{p(1+2\theta)-q}{2(1+3\theta)}, \\[2ex] k'' = \dfrac{3q-p}{2(1+3\theta)}, \end{cases}$$

where
$$p = -\frac{4K(1+3\theta)}{H^2}\sigma + 4\pi k^2 + 3k,$$

$$q = -\frac{2E(1+2\theta)}{H^2}\lambda + \frac{8\pi k^2}{3}(1+\theta) + k.$$

From (e) and (f), we find

$$\text{(C)} \qquad \begin{cases} k' = \left(\delta k - \dfrac{3\lambda\delta I}{\sigma H}\right)\dfrac{K}{\lambda E}, \\[2ex] k'' = -3\left(\dfrac{\delta I}{\sigma H} + k'\right). \end{cases}$$

As these coefficients depend on Young's modulus and on rigidity, it was necessary to determine these constants in the specimens of ferromagnetics used in these experiments. Young's modulus was determined in the usual way from the results of flexure experiments on iron and nickel rods already examined. The modulus of rigidity was found by measurement of the torsion produced by a known twisting couple. For calculating the rigidity from the torsion of a square rod, the following formula, due to Saint Venant,[1] was used.

$$\text{Modulus of Rigidity} = \frac{6 \times \text{Moment of the couple}}{0.843 \times (\text{side of the square})^4 \times \text{angle of torsion}}.$$

Thus we obtain

For	E(Young's modulus)	K(rigidity)	Bulk-modulus	θ
Iron	2.10×10^{12}	0.800×10^{12}	1.88×10^{12}	0.844
Nickel	2.07×10^{12}	0.771×19^{12}	2.16×10^{12}	1.082.

1). Saint Venant. *Torsion des prismes*, p. 336, 1855.

The constants of elasticity for nickel are in fair agreement with Prof. Voigt's[1] determinations, who gives $E=2.03\times10^{12}$, $K=0.782\times10^{12}$.

We now possess sufficient experimental data to calculate the coefficients k' and k''. In finding k' and k'' from experiments on the effects of stress on magnetization, we shall combine the measurements of the changes produced by pull and by hydrostatic pressure. Taking into account the minuteness of the effect of pressure compared to that of pull, we can greatly simplify the calculation.

We know that $\frac{3\delta I}{H\sigma}$ is very small compared to $\frac{\delta k}{\lambda}$; we therefore conclude from (e) that in the combination above mentioned,

$$3k' \doteqdot -k'' \quad ,$$

whence (f) gives for the change of susceptibility due to longitudinal pull

$$\delta k = \frac{\lambda E}{K}.k'.$$

We can thus find k' and k'', without further experiment, by measurement of the effect of longitudinal pull only. The difference in the value of k' caused by neglecting $\frac{3\delta I}{H\sigma}$ is quite within the experimental error, as will be immediately shown.

Results in nickel. As the nature of these coefficients is simpler in nickel than in iron, we shall first give the numbers for the former metal.

The following table contains the numbers obtained from the experimental curves, and used in the calculation of k' and k'' from the strains produced by magnetization.

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1). Voigt, *Wied. Ann.* **49**, 393, 1893.

Table. 1.

H	k	$\frac{\delta l}{l}$	$\frac{\delta v}{v}$	k' (calc.)	k'' (calc.)	$3k'+k''$	$3k'+k''$ $\left(\text{from } \frac{\delta v}{v}\right)$
5	4.20	-2.5×10^{-7}	-0.01×10^{-7}	−14930	+46400	+1610	+ 810
10	9.50	− 7.5	−0.03	−11410	+35760	+1530	+1540
20	8.75	− 20.5	−0.07	− 7800	+24710	+1310	+1340
30	8.10	− 33.8	−0.13	− 5700	+18150	+1050	+1060
40	6.98	− 50.0	−0.22	− 4740	+15040	+ 820	+ 840
50	6.10	− 65.0	−0.34	− 3930	+12470	+ 680	+ 690
100	3.90	−124.0	−1.00	− 1850	+ 5910	+ 360	+ 350
150	2.88	−158.0	−1.59	− 1040	+ 3340	+ 220	+ 230
200	2.27	−175.6	−2.04	− 650	+ 2090	+ 140	+ 150
300	1.59	−201.3	−2.47	− 330	+ 1060	+ 70	+ 80
400	1.22	−214.1	−2.70	− 200	+ 630	+ 30	+ 50
500	0.98	-217.6×10^{-7}	−2.83	− 130	+ 410	+ 20	+ 30

The value of $3k'+k''$ given in the last column were calculated from the change of volume alone. The coefficients k' and k'' are very large in low fields and diminish rapidly as the field is increased. The values of $3k'+k''$ calculated from the strains caused by magnetization show that it is generally very small, satisfying the condition

$$3k' \doteqdot -k''.$$

Since the change of magnetization due to increase of volume σ is $\delta I = -\left(k'+\frac{k''}{3}\right)\sigma$, we see that if $k'+\frac{k''}{3}>0$, there must be increase of magnetization by compression.

Thus, if we accept Kirchhoff's theory, smallness of the volume change by magnetization is necessarily accompanied by the smallness of the effect of hydrostatic pressure, as already verified by experiment; and the strains produced by magnetization in nickel show that the compression must tend to increase the magnetization.

Using the experimental results for the changes of magnetization by longitudinal pulls, 0.19 kg. sq. mm. and 0.38 kg. sq. mm.,

producing the elongations 0.898×10^{-5} and 1.796×10^{-5} resp., we find the following numbers for k' and k'':

Table. 2.

H	k'(0.19 kg. sq. mm.)	k''(0.19 kg.sq.mm.)	k'(0.38 kg.sq.mm.)	k''(0.38 kg.sq.mm.)
10	− 5200	+15600	− 6130	+18390
15	−13390	+40170	− 9980	+29940
20	−11060	+33180	− 8610	+25830
30	− 6740	+20220	− 5650	+16950
40	− 4200	+12600	− 3530	+10590
50	− 3010	+ 9030	− 2290	+ 6870
70	− 1860	+ 5580	− 1180	+ 3540
90	− 1190	+ 3570	− 646	+ 2060
100	− 1000	+ 3000	− 493	+ 1480

The numbers for k' and k'' calculated from the stress effect on the magnetization of nickel is in rough agreement with those deduced from the strain caused by magnetization, the coincidence being closer with smaller loading.

Let us now calculate the strain, which would be produced by magnetization, according to Kirchhoff's theory, from the stress effect, and the stress effect from the strain caused by magnetization. If we adopt the numbers in Table 1, and calculate the change of magnetization due to longitudinal pull, we obtain the following numbers.

H	δI(0.19 kg. sq. mm.)	δI(0.38 kg. sq. mm.)
10	− 2.90	− 5.80
15	− 3.51	− 7.01
20	− 4.00	− 8.00
30	− 4.45	− 8.90
40	− 4.87	− 9.74
50	− 5.05	− 10.10
70	− 5.08	− 10.15
90	− 4.88	− 9.76
100	− 4.80	− 9.60

We now use the numbers in Table 2 and calculate the strain due to magnetization ; we thus obtain—

H	$\frac{\delta l}{l}$ (0.19 kg.sq.mm.)	$\frac{\delta l}{l}$ (0.38 kg.sq.mm.)	$\frac{\delta v}{v}$ (calc.)	$\frac{\delta v}{v}$ (exp.)
10	-3.1×10^{-7}	-3.7×10^{-7}	0.1×10^{-7}	-0.1×10^{-7}
15	-18.9	-14.0	0.2	-0.1
20	-27.7	-21.3	0.3	-0.2
30	-37.5	-31.2	0.6	-0.3
40	-41.3	-34.3	0.7	-0.4
50	-46.0	-34.3	0.9	-0.5
70	-55.3	-33.7	1.2	-0.8
90	-58.1	-29.5	1.5	-1.1
100	-60.2	-27.3	1.6	-1.2

As calculated from the strain effect, the change of magnetization due to longitudinal pull reaches a minimum in a critical field as already verified by experiment ; there is some discrepancy in the actual numbers, but the quality of the change does not show any material difference. The change of length in nickel as calculated from the stress effect fairly agrees with the observed values, except in strong fields, where the deviation becomes apparent. Of the two sets of k', the one derived from the effects of smaller stress gives results which approach the experimental number at least in quality. The agreement between theory and experiment would perhaps be closer, could we measure the change of intensity by still smaller loading ; or better still from effects of small longitudinal compression. Adopting the numbers obtained from the stress effect, the change of volume by magnetization ought to be very small. The discrepancy between theory and experiment lies in the sign ; theory gives increase of volume instead of diminution as in the actual case. But considering the minuteness of the change and the experimental errors which enter in the determination of k' and k'', we can not say that the discrepancy is of a serious nature.

It must not be forgotten that these numbers k', k'' are functions of the strain caused by mechanical action on nickel. Taking Prof. Ewing's experiments on the magnetization of nickel under various loadings, we find the following values of $-k'$ on the supposition that

$$3k'+k''=0.$$

H	5.5 kg.sq.mm.	11 kg.sq.mm.	16.5 kg.sq.mm.	22 kg.sq.mm.	27.5 kg.sq.mm.	33 kg.sq.mm.
30	4250	3620	2950	2350	1680	1170
50	2320	2140	1930	1660	1260	900
100	950	850	810	800	670	520

The above values will probably not be far from those obtained by actual determination. The constants k' and k'' are thus functions of the strain of the magnetized body. In nickel $-k'$ diminishes as the longitudinal pull is increased. In calculating the coefficients from the stress effect, we have taken care to use such values of δI as are due to very small loading, in order that the results may be comparable to those obtained from the strains produced by magnetization.

The diminution of $-k'$ with increased loading is greater in the weak than in strong fields. Applying equation (d) for measuring the length change produced by magnetization, we notice that $\frac{\delta l}{l}$ diminishes with the coefficient k'', so that we expect from the above result the decrease in the contraction of nickel wire with increased longitudinal pull; but as the rate of diminution of k'' becomes less as the field strength is increased, the diminution in the contraction will not be so marked in the strong as in weak fields. This theoretical conclusion is borne out by the experiments of Bidwell on the effect of longitudinal stress on the length change of nickel wire. The change of volume due to magnetization will somewhat diminish for nickel wire under longitudinal pull, but the difference will not be so pronounced

as for the length change. The experimental verification of these conclusions will involve considerable difficulty.

Results in iron.—The experimental and theoretical results are widely discordant in iron. Making use of the measurement of strains in the ovoid caused by magnetization, we find the following numbers for k' and k'' :—

Table. 3.

H	k	$\frac{\delta l}{l}$	$\frac{\delta v}{v}$	k' (calc.)	k'' (calc.)	δI (calculated 0.19 kg.sq.mm.)	δI (experim. 0.19 kg.sq.mm)
10	101.0	$+26.0 \times 10^{-7}$	$+0.79 \times 10^{-7}$	+64600	−74400	+4.30	+ 3.15
15	78.0	+29.4	+0.97	+36800	−29100	+1.97	+ 3.20
20	61.0	+31.5	+1.11	+21100	−19400	+1.97	+ 1.88
30	42.3	+34.0	+1.30	+10090	− 9290	+1.42	+ 0.30
40	32.5	+32.8	+1.41	+ 5650	− 4620	+0.86	− 0.44
50	26.7	+31.8	+1.50	+ 3660	− 2590	+0.53	− 0.73
100	14.5	+24.1	+1.70	+ 870	− 121	−1.74	− 0.98
150	10.0	+16.8	+1.84	+ 353	+ 134	−3.39	.....
200	7.8	+ 9.7	+1.99	+ 183	+ 183	−4.29	.....
300	5.5	− 4.6	+2.28	+ 65	+ 170	−4.97	.....

The above table shows that k' and k'' are of the same order of magnitude as for nickel ; they are, however, for the most part of opposite sign. The approximate relation $k' + \frac{k''}{3} = 0$ does not hold for iron, the quantity $k' + \frac{k''}{3}$ amounting to several thousands in low fields. It would therefore appear that the effect of hydrostatic pressure is considerable, which is irreconcilable with the experiments already cited. For the values of δI in the 7th column, we see that for the small elongation, there is rapid increase of magnetization in low fields, which ultimately reaches the maximum in $H = 10$ nearly ; this point evidently coincides with the Villari critical point. The magnetization then begins to diminish very slowly but continuously till it becomes less than in the unstrained state. This theoretical conclusion agrees

with experiment, although the actual numbers are somewhat different, as will be seen from the last column

If we now make use of the experimental result that the effect of hydrostatic pressure is negligibly small compared with that of the longitudinal, we obtain the following values of $k' = -\frac{1}{3}k''$

Table. 4.

H	k' (0.38 kg. sq. mm.)	$\frac{\delta l}{l}$ (calcul.)	$\frac{\delta l}{l}$ (exp.)	$\frac{\delta r}{r}$ (calcul.)	$\frac{\delta r}{r}$ (exp.)
10	+10000	20.2×10^{-7}	25.5×10^{-7}	11.4×10^{-7}	0.8×10^{-7}
15	+12640	31.9	29.3	17.2	1.0
20	+ 9730	44.6	31.5	16.7	1.1
30	+ 4120	45.2	33.0	18.2	1.3
40	+ 1420	37.4	32.8	18.8	1.4
50	+ 360	30.0	31.8	20.2	1.5
70	+ 100	23.2	28.3	21.4	1.6
90	+ 160	21.7	25.6	24.2	1.7
100	+ 180	17.5	24.0	23.9	1.7

The numbers found above differ widely from those calculated from the strains due to magnetization, but the general character of the coefficient k' is similar. Using the values of k' in Table 4, we find that the change of length given in the 3rd column fairly agrees with the experimental determination in the 4th column. The field of maximum elongation ($H=30$) given by calculation agrees pretty well with the actual result.

According to Kirchhoff's theory, there is always increase of volume with increasing field, but the calculated result is about 15 times greater than the experimental numbers. Thus, the theoretical result as regards the change of volume agrees only in quality.

From experiments on the effect of twist on a circularly magnetized wire, Drude[1] found that in low field $\mu'' = 4\pi k'' = 4 \times 10^5$; here we

1). Drude, *Wied. Ann.* **63**, p. 8, 1897

find it to be about 3.8×10^5 from experiments on the effect of stretching.

Summary.

We conclude the present paper by giving a summary of the results of the research on which it is based.

(1) The volume of iron increases by magnetization.

(2) Diminution of volume by hydrostatic pressure produces decrease of magnetization in iron.

(3) The volume of nickel decreases by magnetization.

(4) Diminution of volume by hydrostatic pressure produces increase of magnetization in nickel.

(5) Positive transverse pressure produces increase of magnetization in an iron tube ; the magnetization reaches a maximum in a critical field, thence to diminish gradually till it ultimately becomes less than in the unstrained state.

The following gives a comparison of Kirchhoff's theory with experiment.

I. Effects of stress calculated from the strains caused by magnetization.

(a) (Theory) Hydrostatic pressure in iron produces increase of magnetization.

(Experiment) Hydrostatic pressure produces diminution of magnetization in iron.

(b) (Theory and Experiment) Hydrostatic pressure produces small increase of magnetization in nickel.

(c) (Theory and Experiment) By the application of a small constant longitudinal pull, there is increase of magnetization in iron till it reaches a maximum in moderate field, thence to diminish till the magnetization becomes smaller than in the unstretched condition.

(d) (Theory and Experiment) By the application of a small constant longitudinal pull, there is decrease of magnetization in nickel till it reaches a minimum in moderate field, thence to increase gradually, but not to such a degree as to reach a value greater than in the unstretched condition.

II. Strains caused by magnetization calculated from the effects of stress.

(a) (Theory and Experiment) Magnetization produces increase of volume in iron. (But the value assigned by theory is about 15 times greater than the observed result).

(b) (Theory) Magnetization produces a small increase of volume in nickel (to a degree which is quite within the experimental error).

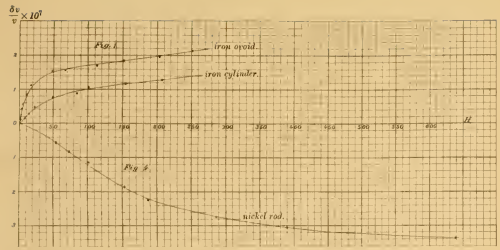
(Experiment) Magnetization produces diminution of volume.

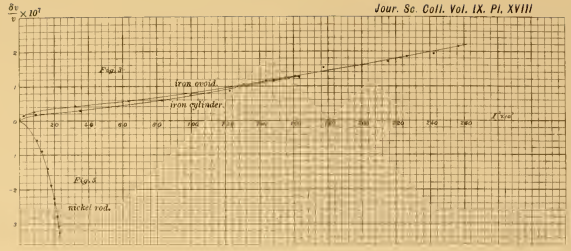
(c) (Theory and Experiment) Magnetization produces increase of length in iron, till it reaches a maximum in a critical field ($H=30$), thence to diminish gradually with increasing field.

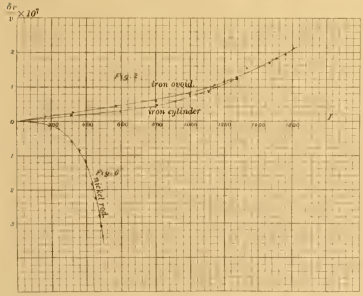
(d) (Theory and Experiment) Magnetization produces continuous diminution of length in nickel.

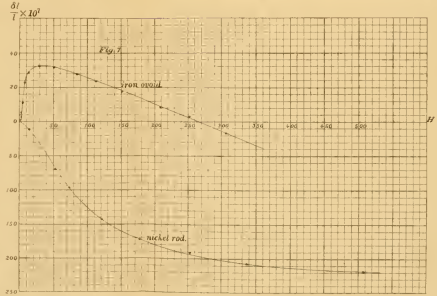
Experiments show that the coefficients k' and k'' are complicated functions of the strain, but Kirchhoff's theory makes the change of magnetization simply proportional to the strain. Strictly speaking Kirchhoff's theory is a rough approximation, and will perhaps only hold when the strain is infinitely small; we can not therefore, expect that such a theory will explain all the relations between the strains caused by magnetization and the effects of stress on magnetization in all their qualitative and quantitative details. In the present investigation, we have taken care to measure such effects as will be most conformable to the theory. We have thus found out that, excepting the theoretical deduction as to the effect of hydrostatic

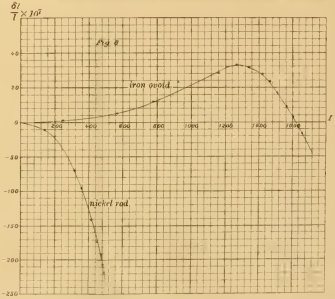
pressure on the magnetization of iron, there are no serious discrepancies between theory and experiment. In default of a more perfect theory, it will be of no small interest to see how far the aforesaid theory can explain the correlation of strain and stress in magnetization; we intend to continue our investigations into the Wiedemann effect, and see to what extent the mutual relations between the strain due to magnetization and the effects of stress on the magnetization can be traced.


δv/v × 10⁷
Fig. 1.
iron ovoid.
iron cylinder.
H
Fig. 4.
nickel rod.


δv/v × 10⁷
Fig. 2.
iron ovoid.
iron cylinder.
I
Fig. 5.
nickel rod.


δr/r × 10⁷
Fig. 3.
iron ovoid.
iron cylinder.
I
Fig. 6.
nickel rod.


δl/l × 10⁷
Fig. 7.
iron ovoid.
H
nickel rod.


δl/l × 10⁷
Fig. 8.
iron ovoid.
I
nickel rod.

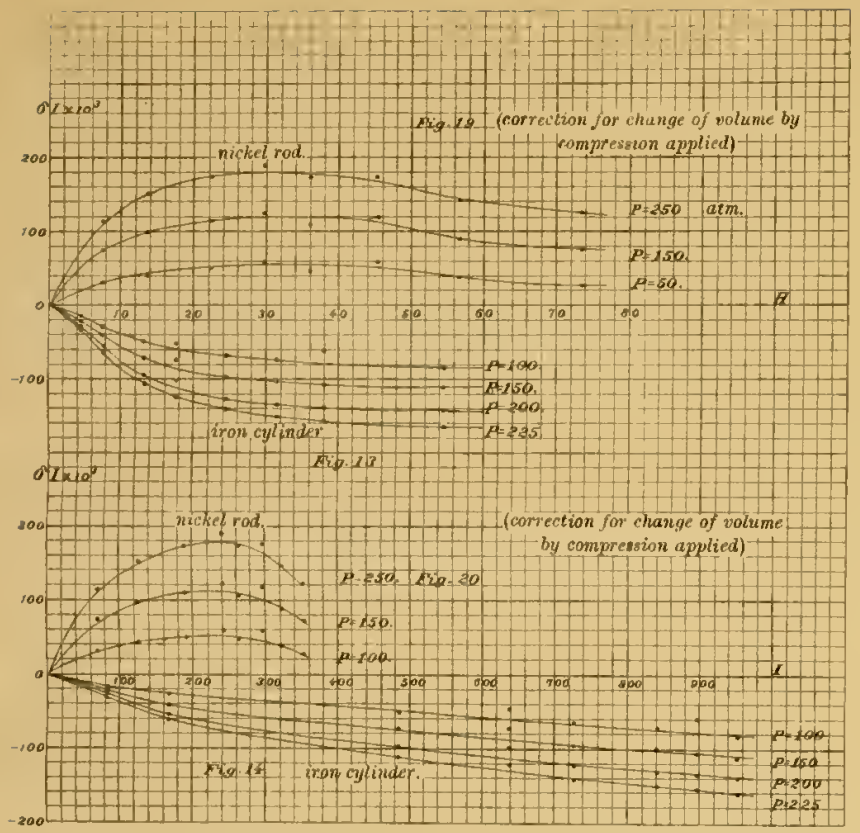


Fig. 19 (correction for change of volume by compression applied)
nickel rod.
P=250 atm.
P=150.
P=50.
P=100.
P=150.
P=200.
P=225.
iron cylinder
Fig. 13
nickel rod.
(correction for change of volume by compression applied)
P=250. Fig. 20
P=150.
P=100.
P=100
P=150
P=200
P=225
Fig. 14
iron cylinder.

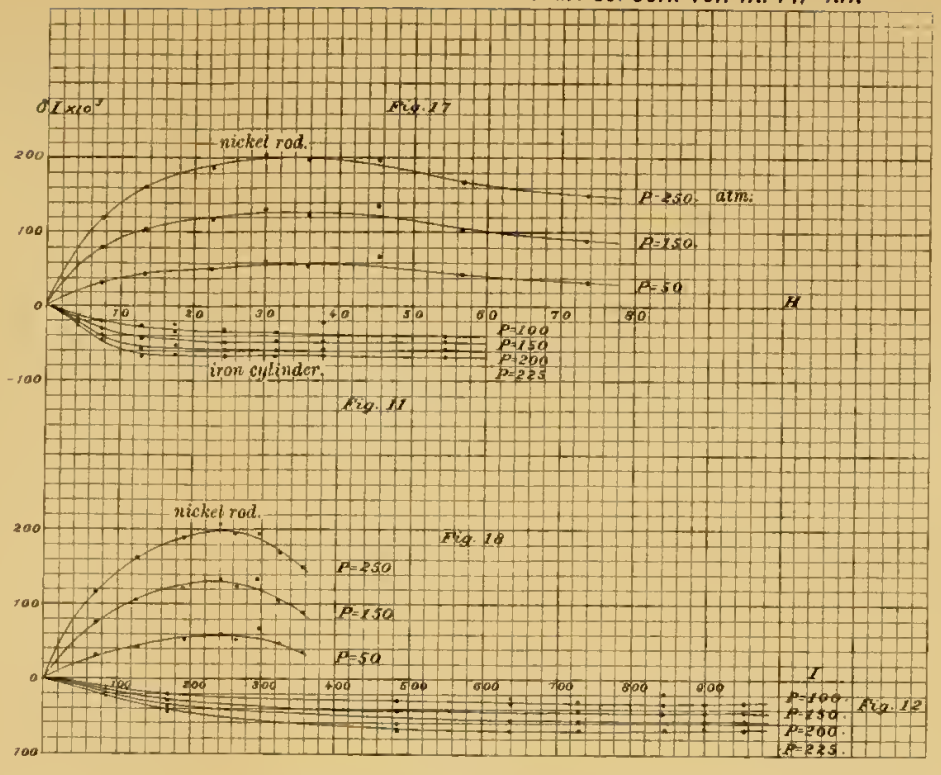


Fig. 17
nickel rod.
P=250. atm.
P=150.
P=50
P=100
P=150
P=200
P=225
iron cylinder.
Fig. 11
nickel rod.
Fig. 18
P=250
P=150
P=50
P=100
P=150
P=200
P=225
Fig. 12

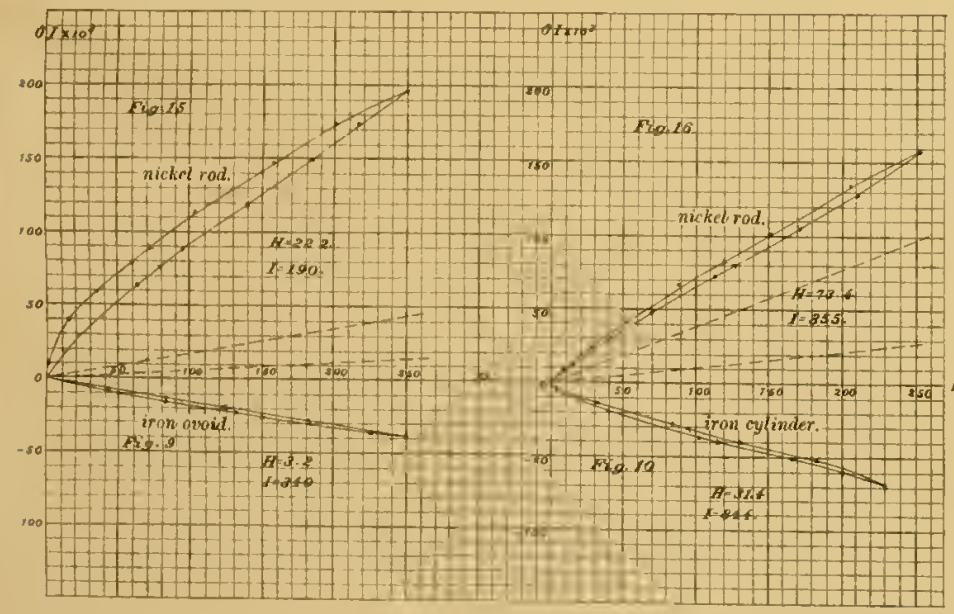
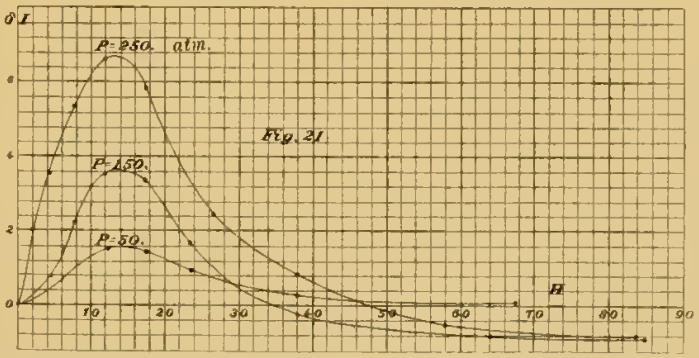


Fig. 15
nickel rod.
H=22.2
I=190.
iron ovoid.
Fig. 9
H=3.2
I=340
Fig. 16
nickel rod.
H=73.4
I=855.
iron cylinder.
Fig. 10
H=31.4
I=844.


P=250. atm.
Fig. 21
P=150.
P=50.

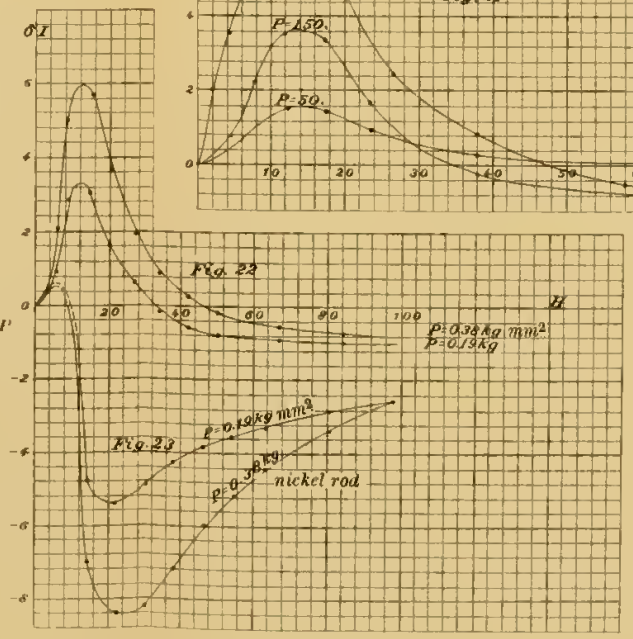


Fig. 22
P=0.38kg mm²
P=0.19kg
Fig. 23
P=0.19kg mm²
P=0.38kg
nickel rod

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ERRATA.

Pg. 339, line 10.

for $l=\dfrac{1-\sqrt{k'}}{1+\sqrt{k}}$, $l_1=\dfrac{1-\sqrt{k}}{k+\sqrt{k}}$

read $l=\dfrac{1-\sqrt{k'}}{1+\sqrt{k'}}$, $l_1=\dfrac{1-\sqrt{k}}{1+\sqrt{k}}$

Pg. 339, line 14.

for $K=\dfrac{\pi}{2}(1+2h+2h^4+2h^9+\ldots\ldots\ldots\ldots)$

read $K=\dfrac{\pi}{2}(1+2h+2h^4+2h^9+\ldots\ldots\ldots\ldots)^2$

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